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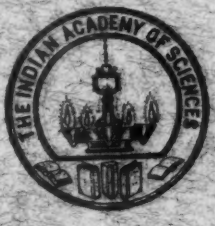

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CHEMISTRY OF PONGAMOL. PART I

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Received January 10, 1942

The discovery of a new crystalline compound from the oil of *Pongamia glabra* was announced in a communication sent to *Current Science*.[1] The remarkably bright colours which it yields with ferric chloride and with concentrated sulphuric acid gave a clue to the existence of this compound in the oil. Compared with karanjin it is a minor component, far more soluble in oils, less bitter and less toxic to fish.[2] Owing to the difficulties of isolation of the substance in a pure condition and the complexity of its reactions the problem of elucidating its constitution has proved to be difficult and slow in progress. We are therefore presenting in this paper the important results obtained so far.

The results of combustion analysis suggest the formula $C_9H_7O_2$ and a determination of the molecular weight indicates that the molecular formula should be just double this, $C_{18}H_{14}O_4$. This is further supported by the analysis for the methoxyl group and calculation for the weight of the compound containing one methoxyl.

Though from the reaction of the compound with ferric chloride the presence of a phenolic or enolic group is definite, isolation of a derivative in a pure condition has not been possible, since the methyl ether, acetate and benzoate came mostly as liquids in small quantities. The *p*-nitro-benzoyl derivative was obtained tolerably pure and its analysis supported the above formula.

Demethylation of pongamol has given rise to somewhat anomalous results and two products have been obtained by using different demethylating agents. By the action of hydrobromic acid and acetic anhydride and also by the action of hydriodic acid the same compound (I) resulted. Though this gave a slightly low carbon value on analysis, it agreed with the expected value for the simple demethylation product fairly satisfactorily. But the substance behaved extraordinarily in its reactions since it gave no colour with ferric chloride and was insoluble in alkali. With aluminium chloride, however, demethylation proceeded differently and the nor-pongamol (II) so obtained was readily soluble in alkali and gave satisfactory analytical results. It may

be tentatively stated that aluminium chloride brings about a simple demethylation whereas the halogen acids carry the reaction further in a manner which is not at present clear.

By the action of bromine in glacial acetic acid pongamol gave rise to a bromo-derivative which contained four bromine atoms in the molecule ($C_{18}H_{14}O_4Br_4$). It did not give any of the colour reactions of pongamol with ferric chloride or sulphuric acid. At least a portion of the bromine seemed to be held in a loose condition since on boiling the compound with acetone the evolution of bromo-acetone could be noticed. From the analytical results it could be concluded that the resulting compound had the formula $C_{18}H_{13}O_4Br_3$.

Oxidation of pongamol with potassium permanganate proceeded very smoothly and rapidly and about 30% yield of benzoic acid was obtained. Further the substance gave an orange red colour on reduction with magnesium and alcoholic hydrochloric acid; by the action of sodium amalgam and subsequent acidification with strong mineral acid a red colour which faded slowly was obtained. These results indicate that pongamol belongs to the flavone group of compounds. It has also been noticed that in the Wilson's boric acid test[3] using a mixture of boric and citric acids in acetone solution, though there was no immediate formation of colour, a distinct yellow colour developed when the mixture was allowed to stand for about half an hour; this colour became more and more intense on further keeping. The significance of this observation is not very clear at present.

Degradation with alkali has again proved to be complex. Though pongamol does not dissolve easily in cold aqueous potash, it does so on warming and rapidly undergoes decomposition. Amongst the products obtained, the presence of benzoic acid is definitely established. The others are being studied.

Experimental

As has been described elsewhere,[2] pongamol was found to be present in the pongamia oil obtained by pressing or by solvent extraction and in the press-cake. However experience showed that the most convenient source for getting the compound in appreciable quantity was a stale sample of the expressed oil from which karanjin, together with free fatty acids, had been removed by a process of natural deposition. This oil (1 litre) was extracted with methylated spirit continuously in a special apparatus for about 40 hours. The solvent was distilled off from the extract as far as possible, when a yellow solid mixed with some oil was obtained. In case no solid separated as above the thick oily residue was allowed to stand for a few days; thereupon

big crystals usually separated from the oil. In either case the purification of the solid was effected by treating the magma with a little ether when the oily portion alone dissolved. After decanting off the ether solution and repeating the operation a few more times a pure solid melting at 123° was obtained (yield 1 gm.). Crystallisation of this from alcohol-acetic acid mixture gave pongamol as large pale yellow crystals (rhombic prisms) melting at 128–29°. A mixed melting point with karanjin (m.p. 158°) was considerably depressed (Found: C, 73·6, 73·5; H, 4·5, 5·0; OCH_3, 10·5; $C_{19}H_{14}O_4$ requires C, 73·5; H, 4·8; OCH_3, 10·5%.)

The compound was insoluble in water, sparingly soluble in alcohol and moderately soluble in acetic acid. Aqueous sodium hydroxide did not dissolve it in the cold but decomposed it readily on boiling with the production of aromatic odour. Pongamol dissolved in concentrated sulphuric acid to give a yellow solution which turned deep emerald green in the course of five minutes. The fresh yellow solution in this acid also exhibited a green fluorescence which was rapidly lost. An alcoholic solution of pongamol gave an intense red colour with ferric chloride.

The molecular weight of pongamol was first determined by Rast's method using camphor as the solvent. But the result did not correspond to either of the formulæ $C_9H_7O_2$ or $C_{18}H_{14}O_4$. A value falling into line with the empirical formula and with the methoxyl content was, however, obtained by the cryoscopic and ebullioscopic methods using benzene as the solvent [Found: by Rast's method 220, by cryoscopic method 280, by ebullioscopic method 300. $C_9H_7O_2 = 147$; $C_{18}H_{14}O_4 = 294$; minimum molecular weight from methoxyl content (10·5%) = 295.]

Acetylation of pongamol was attempted using acetic anhydride and sodium acetate. After boiling for 5 hours the mixture was poured into excess of cold water and allowed to stand overnight. Only a liquid product was left behind which did not solidify even after prolonged standing in the refrigerator. It was easily soluble in methyl alcohol but no solid could be obtained from this solution by any means.

The methylation of pongamol using potassium carbonate and excess of methyl iodide in boiling acetone solution gave rise to a product which remained a viscid liquid even after repeated attempts to purify it by means of organic solvents. The benzoylation was similarly carried out by treating pongamol with benzoyl chloride in boiling benzene solution. After distilling off most of the solvent and decomposing the excess of benzoyl chloride with water the mixture was ether extracted and the extract shaken with an aqueous solution of sodium bicarbonate to remove benzoic acid. The residue obtained by distilling off the solvent was also a viscid liquid which could not be

converted into the solid form by crystallisation from solvents. The use of pyridine in small quantities as a condensing agent or in larger quantities as a solvent did not make any difference.

A greater measure of success, however, attended the preparation of the *p*-nitrobenzoate which was accomplished as follows. The compound (0·5 gm.) dissolved in benzene (10 c.c.) was treated with *p*-nitrobenzoyl chloride (0·5 gm.) and the mixture was heated under reflux on a boiling water-bath for about 12 hours. The solution gradually acquired a dark green colour. It was then poured into an evaporating basin and left in a good draft of air to get rid off as much of the solvent as possible. The residue was treated with dilute aqueous sodium carbonate and the mixture repeatedly ether extracted. The filtered ethereal solution was shaken with dilute sodium hydroxide solution to remove any free nitrobenzoic acid and then evaporated. The sticky solid thus obtained was extracted with small portions of hot alcohol. The first extract which was very dark yielded a small quantity of crystalline solid mixed with resin; this was discarded. The subsequent extracts gave a purer sample which was crystallised form aqueous acetic acid. Though fairly crystalline in appearance the crystal form was indefinite and the solid did not possess a definite melting point. It was free from traces of the original compound since it did not give a ferric chloride colour. It was therefore macerated with aqueous sodium carbonate to remove any traces of nitrobenzoic acid and left overnight in contact with the alkali and then filtered and washed with water and finally crystallised from dilute acetic acid. The melting point, however, was still indefinite. The *p*-nitrobenzoate melted at 200–5° with sintering at about 105° and when it was examined under the microscope rectangular rods and needles could be seen along with some nodules. (Found: C, 66·6; H, 3·8; $C_{25}H_{17}O_7N$ requires C, 67·7; H, 3·8%.) Experiments using pyridine as the condensing agent were unsuccessful.

Oxidation with alkaline permanganate.

The compound (1 gm.) was dissolved in 5% aqueous potassium hydroxide (50 c.c.) with warming and shaking for about half an hour. The solution was then treated with 4% potassium permanganate solution (100 c.c.), added slowly during two hours with continuous shaking. Much warmth was produced throughout the addition. After leaving overnight the mixture was treated with excess of sulphur dioxide when a clear solution was obtained. It was filtered off from a small quantity of resinous material with the help of a fluted filter and then concentrated under reduced pressure. When the residual liquid began to turn turbid, distillation was stopped. A fair amount of a white solid separated from the liquid overnight. The filtered solution was repeatedly ether-extracted and the combined ether extract

concentrated by distillation until a thick liquid was obtained. This liquid, however, rapidly deposited big colourless prismatic crystals which were carefully ladled off and freed from traces of adhering liquid by pressing on the porous tile. The crystals now melted at 118–19° and were found to be those of benzoic acid.

The liquid, from which the above crystals separated, slowly solidified in half an hour. This solid on crystallisation from hot water also yielded benzoic acid melting at 115°. The total yield of benzoic acid in this experiment was 0·3 gm.

Demethylation of pongamol.

Using hydriodic acid.—Finely powdered pongamol (0·5 gm.) was gently boiled with hydriodic acid (d. 1·7, 15 c.c.) for 5 hours. The mixture was then diluted with water (20 c.c.), when a dark solid separated from the deeply coloured solution. On passing sulphur dioxide the solution lost most of its colour but the dark solid was practically unaffected. After pouring out the aqueous solution the solid was extracted with hot pyridine and the decanted pyridine solution treated with a little water. The black sticky solid that separated was discarded. Further addition of water to the hot solution deposited some more of this substance. The final aqueous pyridine solution gave on cooling a mass of woolly needles melting at 119–20°. On repeated recrystallisation from alcohol in which it was easily soluble it was obtained as long colourless needles melting at 145–46°. It was free from methoxyl groups; still it did not dissolve in cold aqueous sodium hydroxide and was only slowly dissolved on warming, with the production of an aromatic smell due to decomposition. Alcoholic ferric chloride gave no colour. Sulphuric acid gave a very pale yellow solution devoid of fluorescence whereas an alcoholic solution exhibited a blue fluorescence. (Found: C,72·1, 72·1; H, 4·8, 4·1; $C_{17}H_{12}O_4$ requires C = 72·9, H = 4·3%.)

Using aluminium chloride.—The compound (0·3 gm.) dissolved in benzene (30 c.c.) was treated with freshly powdered anhydrous aluminium chloride (3 gm.) and the mixture was kept gently boiling under reflux on a water-bath for about 40 minutes. The benzene was then distilled off and the residue treated with hydrochloric acid (1:1). The residual solid was filtered, washed with dilute hydrochloric acid and then with water and crystallised twice from alcohol. A yellow powder (plates and needles under the microscope) melting at 224–5° was thus obtained. It contained no methoxyl, dissolved in cold alkali giving a deep yellow solution and gave a pale green ferric chloride colour. Concentrated sulphuric acid dissolved it to give a colourless solution with a blue fluorescence. (Found: C, 72·7; H, 4·7; $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%.)

Action of bromine.

Pongamol (0·3 gm.) was dissolved in glacial acetic acid (7 c.c.) and treated with a solution of bromine in the same solvent. The absorption of bromine was rapid in the beginning. Excess of the reagent was added and the mixture which had warmed up perceptibly was left well stoppered at the laboratory temperature for 5 hours with occasional shaking. It was then poured into a large excess of water (200 c.c.) when a light precipitate was immediately formed. The supernatant liquid which was highly coloured owing to the excess of bromine used, slowly became less and less coloured as the mixture was left exposed to the air. The white solid was filtered after some hours and washed with plenty of water. Recrystallisation from solvents was not feasible since on warming a paste was invariably produced. The dry sample sintered at about 70° and slowly decomposed above 125°. (Found in the air-dried specimen: C, 36·3; H, 2·5, Br, 51·4; $C_{18}H_{14}O_4Br_4$ requires C, 35·2; H, 2·3; Br, 52·1%.) It gave no colour with alcoholic ferric chloride and in sulphuric acid it dissolved rather slowly to give a very pale yellow solution.

Action of boiling acetone on the above bromo compound.

The tetrabromo compound (0·5 g.) was suspended in acetone (10 c.c.) and heated on a warm water-bath under reflux. Most of the solid dissolved in the solvent to give a pale yellow solution by the time boiling commenced; the remaining solid also went into solution in the course of ten minutes giving rise to a clear orange red solution. After boiling for one hour the solvent was distilled off from the water-bath as far as possible. The last portions of the distillate as also the residue had a very irritating smell and were highly lachrymatory, obviously due to the formation of bromoacetone. The residual oil was freed from bromoacetone still remaining in it by boiling with water and decanting off the clear aqueous portion while hot. After a second repetition of the process the aqueous extract was no longer lachrymatory and the warm plastic mass hardened to a solid on cooling. On gentle rubbing with a glass rod this disintegrated to a yellow powder.

Purification of the solid thus obtained was attempted using alcohol as the solvent, but the alcoholic solution did not deposit any solid on cooling. Addition of a small amount of water caused the separation of an oil which did not solidify on keeping. Hence the mixture was largely diluted with water and after standing for some time the aqueous portion was decanted off. Repetition of this washing with excess of water a number of times finally gave rise to a solid yellow powder which was filtered off. The substance thus got sintered at 65°, melted at 83° and decomposed vigorously at 100°.

It was microcrystalline in appearance and gave a yellow solution with sulphuric acid. The pale yellow solution in alcohol gave a brown-red colour with ferric chloride. (Found: C, 40·9; H, 3·0; Br, 44·0; $C_{18}H_{13}O_4Br_3$ requires C, 40·5; H, 2·4; Br, 45·0%.)

Summary

Pongamol, which is the second important crystalline component of the pongamia oil, has the molecular formula $C_{18}H_{14}O_4$ and contains a methoxyl group. It has also a phenolic or enolic hydroxyl group. Demethylation with aluminium chloride yields nor-pongamol whereas treatment with hydriodic acid gives rise to a product which is probably isomeric but does not possess phenolic properties. Treatment with bromine produces a tetrabromo derivative which on boiling with acetone yields a tribromo compound. Oxidation with potassium permanganate or decomposition with alkali yields benzoic acid. From these properties and from colour reactions it is suggested that pongamol is a flavone derivative containing a hydroxyl, a methoxyl and an ethylene double bond.

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THE REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED UNSATURATED CARBONYL COMPOUNDS

Part VIII. Addition of Cyanoacetamide to Umbelliferone and its Methyl Ether

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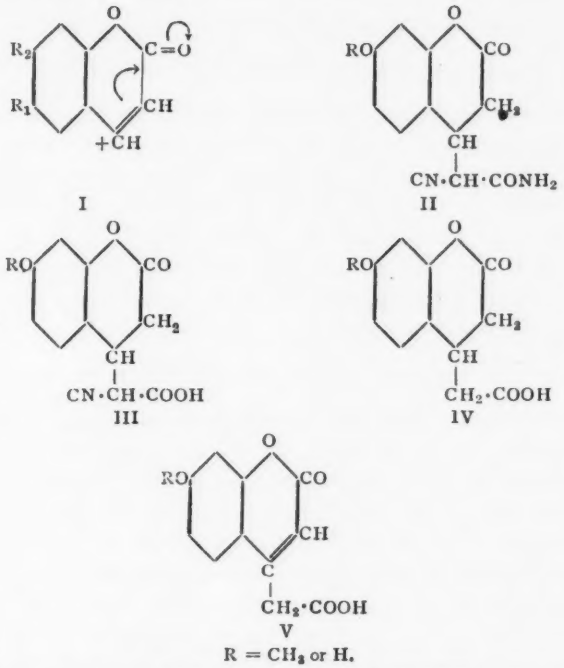
From the results presented in Part I,[1] certain conclusions could be arrived at regarding the influence of substituents on the addition of cyanoacetamide to the double bond in coumarins. Substituents in the pyrone ring completely prevent addition; but their presence in the benzene ring does not produce such great influence. Nevertheless, they seem to effect some control over the reaction. For example, it was noticed that a nitro group in the 6th position speeds up the addition considerably, whereas a methyl group in the 7th position slows it markedly. These findings are in accordance with expectations, since the kationoid reactivity of the carbon atom in position 4 arises according to the mechanism given below (I) and it is the reactive centre promoting the addition of cyanoacetamide. A nitro group in the 6th position as in nitro coumarin (I, $R_1 = NO_2$, $R_2 = H$), can increase the kationoid activity both by its direct effect on the carbon atom in position 4 and also indirectly by influencing the oxygen atom which is linked to the phenyl ring. Groups that can act as electron sources such as methyl when present in the 7th position as in 7-methyl-coumarin (I, $R_1 = H$, $R_2 = CH_3$) produce the opposite effect and consequently reduce the reactivity of the pyrone double bond. This conclusion is now further supported by the experiments on 7-methoxy and 7-hydroxy coumarins described in this paper. They react very slowly producing about 90% yield, the time taken being 50 hours for the methoxy compound, and 120 hours for the hydroxy compound. Larger quantities of the catalyst (1 c.c.) are also required. On the hydrolysis of the methoxy compound (II), both the dihydro-coumarin cyanoacetic acid (III) and the dihydro-coumarin acetic acid (IV) derivatives could be obtained, whereas only the latter could be isolated from the hydroxy compound. The methoxy and hydroxy-dihydro-coumarin acetic acids have also been prepared by the reduction of 7-methoxy and 7-hydroxy

coumarin 4-acetic acids (V) using sodium amalgam. There is thus independent confirmation for the addition of cyanoacetamide to the pyrone double bond in coumarins.



The above compounds form a series of dihydro-coumarin derivatives useful for the study of fluorescence in relation to chemical constitution which is in progress in these laboratories.

Experimental

7-Methoxy-3 : 4-dihydro-coumarin-4-cyanoacetamide (II).—

A solution of 7-methoxy coumarin (2·0 g.), cyanoacetamide (1·2 g.) and piperidine (1·0 c.c.) in alcohol (30 c.c.) was kept boiling for 50 hours. After the end of about 25 hours an insoluble solid began to separate out and the yield of the product was only 0·7 g. The boiling was continued for a further 25 hours when the total yield of the product amounted to 2·7 g. (about 90%). Boiling for longer hours did not improve the yield to any considerable extent. The solid was filtered from the mother-liquor, and washed with hot alcohol to remove unchanged 7-methoxy coumarin. It was insoluble in alcohol, benzene or chloroform and was crystallised from aqueous

pyridine when it came out as lustrous rectangular plates melting at 262–63°. (Found: C, 57·8; H, 5·1; $C_{13}H_{12}O_4N_2$, $\frac{1}{2}$ H_2O requires C, 58·0; H, 4·8%.) The substance dissolves in dilute sodium hydroxide slowly in the cold and readily on boiling to form a yellow solution without fluorescence. It does not exhibit any fluorescence in concentrated sulphuric acid.

7-Methoxy-3 : 4-*dihydro-coumarin*-4-*cyanoacetic acid* (*III*).—

A mixture of 7-methoxy -3 :4-dihydro-coumarin-4-cyanoacetamide (1·0 g.) and cold concentrated hydrochloric acid (6 c.c.) was vigorously shaken, giving a clear solution which soon deposited a colourless crystalline precipitate. It crystallised from much water or aqueous alcohol in long colourless rectangular plates, melting at 247–49°. (Found: C, 59·8; H, 4·2; $C_{13}H_{11}O_5N$ requires C, 59·8; H, 4·4%.) It gives a colourless solution in concentrated sulphuric acid, alcohol or aqueous sodium hydroxide and exhibits no fluorescence in any of the above solutions.

7-Methoxy-3 : 4-*dihydro-coumarin*-4-*acetic acid* (*IV*, $R = CH_3$).—

(*a*) *By hydrolysis.*—This can be obtained by further hydrolysing the above compound with hydrochloric acid. 7-Methoxy-3 : 4-dihydro-coumarin-4-cyanoacetamide (1·0 g.) was boiled with 10 c.c. of concentrated hydrochloric acid for five minutes and the clear solution was evaporated to dryness on a water-bath. The residue was treated with a few drops of water to dissolve the ammonium chloride and the viscous liquid left behind, was allowed to solidify during the course of 2 days. The solid product was crystallised from hot water, using a little animal charcoal, when it came out in long colourless rectangular plates melting at 122–23°. (Found: C, 61·2; H, 5·2; $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1%). The substance dissolves easily in sodium carbonate or sodium hydroxide, and the solution which is at first colourless changes to yellow on standing. The solutions in concentrated sulphuric acid, alcohol, or in dilute aqueous alkali give no fluorescence.

(*b*) *By reduction of 7-methoxy-coumarin-4-acetic acid.*—7-Methoxy-coumarin-4-acetic acid prepared according to the method of Dey and Row[2, 4] was dissolved in absolute alcohol, treated with sodium amalgam (2·5%, 25 g.) and the mixture was kept at a temperature of 50–60° for a period of about three days. Disappearance of fluorescence of the alcoholic solution on dilution with water indicated complete reduction of the compound. The mercury was then separated and the solution was concentrated to a small volume under reduced pressure. Finally it was acidified with dilute sulphuric acid, filtered, and the clear solution was repeatedly extracted with ether. A liquid was obtained on the evaporation of the ether and it solidified in the

course of 4 days. The solid was repeatedly recrystallised from boiling water using a little animal charcoal, when it came out in the form of long colourless rectangular plates melting at 122–23°. It agreed in all properties with the sample obtained by the method of hydrolysis and did not exhibit any fluorescence in concentrated sulphuric acid, alcohol or in dilute aqueous alkali. The mixed melting point was undepressed.

7-Hydroxy-3: 4-dihydro-coumarin-4-cyanoacetamide (II, R = H).—

A solution of 7-hydroxy-coumarin (2·0 g.), cyanoacetamide (1·2 g.) and piperidine (1·0 c.c.) in alcohol (30 c.c.) was kept boiling for about 120 hours. A good yield of the product could be obtained only on boiling for a very long time, the yield being 6% in 25 hours, 20% in 50 hours, 55% in 100 hours and finally 90% in 120 hours. The solid was filtered and washed with plenty of hot alcohol to remove unreacted umbelliferone (m.p. 254-57°). It was finally crystallised from aqueous pyridine when it came out as small rectangular plates which neither melted nor decomposed below 300°. (Found: C, 56·2; H, 4·0; $C_{12}H_{10}O_4N_2$, $\frac{1}{2}$ H_2O requires C, 56·5; H, 4·3%.) The product was insoluble in alcohol, chloroform or benzene. A reddish-brown solution is formed in dilute aqueous sodium hydroxide slowly in the cold and readily on heating, ammonia being evolved.

7-Hydroxy-3: 4-dihydro-coumarin-4-acetic-acid (IV, R = H).—

(*a*) *By hydrolysis.*—7-Hydroxy-3: 4-dihydro-coumarin-4-cyanoacetamide (1·0 g.) was treated with concentrated hydrochloric acid (10 c.c.) and heated on a water-bath till a clear solution was obtained (about 3 minutes). When the solution was evaporated to dryness, it left a crystalline product which was treated with a few drops of water to dissolve the ammonium chloride formed. The remaining solid was crystallised from hot water using a little animal charcoal when it came out in the form of colourless hexagonal tablets, melting at 180–81°. (Found: C, 58·9; H, 4·8; $C_{11}H_{10}O_5$ requires C, 59·4; H, 4·5%.) The substance did not exhibit any fluorescence in concentrated sulphuric acid, alcohol or dilute aqueous alkali.

(*b*) *By reduction of 7-Hydroxy-coumarin-4-acetic-acid.*—7-Hydroxy-coumarin-4-acetic acid prepared according to the method of Dey and Row,[2, 3] was reduced in the manner described in the case of the 7-methoxy compound. The reduction took about five days, the absence of any fluorescence on dilution of the alcoholic solution with water being taken as completion of the reaction in this case also. The compound (m.p. 180–81°) was similar in all its properties with the sample obtained by hydrolysis and the mixed melting point was undepressed.

Summary

The addition of cyanoacetamide to the double bond of 7-methoxy and 7-hydroxycoumarins is very slow and it is attributed to the influence of the substituents which act as electron sources. On hydrolysis, the products yield the corresponding cyanoacetic acid and acetic acid derivatives the latter of which could also be obtained by the reduction of methoxy and hydroxy coumarin-4-acetic acids using sodium amalgam. These compounds do not fluoresce in solution.

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CHEMICAL EXAMINATION OF INDIAN LICHENS

Part V. Occurrence of Active Montagnetol in *Roccella montagnei*

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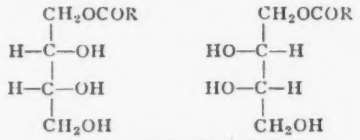
The isolation of montagnetol, a new phenolic component of *Roccella montagnei* and the establishment of its constitution as the erythrityl ester of orsellinic acid were described in two previous publications.[1] In the course of our attempts to prepare large quantities of this substance, a sample of montagnetol was obtained which melted sharp at 135–36° and the melting point could not be raised by repeated purification by the methods already described. Further, crystal form was different, being very small truncated prisms and triangular plates. Otherwise it had the same composition as montagnetol and resembled it very closely in all properties and reactions, and gave the same products of decomposition and synthesis. Thus with hot baryta or dilute sulphuric acid it gave orcinol and erythritol ; it condensed with ethylacetoacetate to form 4 : 7-dimethyl-5-OH-coumarin ; with concentrated sulphuric acid it formed orsellinic acid and erythritol and with methyl alcoholic potash methyl orsellinate and erythritol, and finally as a result of methylation with diazomethane and treatment with alcoholic potash the dimethyl ether of methyl orsellinate and subsequently the dimethyl ether of orsellinic acid could be prepared. It was obvious therefore that the new compound is a stereoisomer of montagnetol, and this idea was confirmed by an examination of the optical activity of the two compounds. The lower melting compound was dextrorotatory, $[\alpha]_D$, +16·0° in water and +12·6° in acetone whereas the higher melting substance was optically inactive. Hence it has been concluded that the former is *d*-montagnetol, and the latter is the racemic variety. The final proof of this relationship was obtained when *d*-montagnetol was converted into the racemic variety by boiling with water for 3 hours. It may be mentioned at this stage that on a few occasions we met with samples of montagnetol having indefinite melting points and with low rotatory power being obviously mixtures of the active and racemic montagnetols. They could be readily converted into the higher melting inactive compound by heating with water as mentioned above.

Though the erythritol present in the two montagnetols belongs to the inactive meso variety the occurrence of optical activity in montagnetol is

easily explicable since dissymmetry is introduced due to esterification of one of the hydroxyl groups of the alcohol as represented below. For the sake of simplicity the hydroxyl involved is arbitrarily taken as that attached to carbon atom number one. The position is in no way affected even if any other hydroxyl were involved.



R = orcinol residue, $C_7H_7O_2$.

In most cases of plant products the optically active compound is of common occurrence and racemisation is brought about during extraction and subsequent treatment. With a view to be precise on this point in regard to montagnetol a number of lichen samples of *Roccella montagnei* were analysed carefully. From some the *d*-variety was isolated with ease. Hence it could be concluded that the method of extraction had no racemising influence. In some other cases a mixture was obtained and the racemic sample was also isolated in some others. It looks therefore that racemisation of montagnetol is taking place even in the plant.

Experimental

The isolation of *d*-montagnetol was made following the same procedure as was adopted for the racemic compound. When obtained from the mixture of solvents, acetone-ether-benzene, the crystals were very small and the structure was not definite. The substance, however, crystallised from acetone on careful addition of benzene in the form of colourless truncated prisms and triangular plates. When mounted on a slide with a drop of water it quickly dissolved and when the solvent evaporated it crystallised as soft fibrous needles. In contrast to this *r*-montagnetol was less soluble and exhibited great tendency to come out in the form of big crystals; it appeared as big rectangular tablets when crystallised from acetone and as lens-shaped crystals when mounted with water. *d*-Montagnetol melted at 135-36° and repeated purification and crystallisation did not raise the melting point. A mixture of it with the higher melting montagnetol melted indefinitely between 130° and 150°. (Found: C, 53·4; H, 6·4; and molecular weight 285. $C_{12}H_{16}O_7$ required C, 52·9; H, 5·9% and molecular weight 272.) Its chemical properties and reactions were just the same as those of *r*-montagnetol.

Optical activity of the two montagnetols.—0·5875 g. of the lower melting montagnetol was dissolved in 25 c.c. of distilled water, a part of the solution

ERRATUM

Vol. XV, No. 1, page 19, *for* ' $mesH_1KOH$ ' *read* ' meoH, KOH '

taken in 100 mm. tube and the rotation observed. It was found to be dextrorotatory, and the specific rotation was $+16{\cdot}2°$. A similar solution in acetone gave $[\alpha]_D$, $+12{\cdot}6°$.

0·5112 g. of the higher melting montagnetol was dissolved in 25 c.c. of distilled water, and a part of the solution taken in a 100 mm. tube. There was no rotation.

Conversion of d-*montagnetol into the racemic compound.*—A solution of the lower melting montagnetol (*d*), (0·8 g. in 25 c.c. of water) was boiled for 3 hours. Racemisation was complete by this time since optical activity disappeared. It was then concentrated when an almost pure sample of the higher melting montagnetol was obtained in a quantitative yield. After one crystallisation from acetone-ether-benzene mixture it melted at 155–56°. Mixed melting point with an authentic specimen of the higher melting compound showed them to be identical.

Summary

A lower melting sample of montagnetol has been isolated from *Roccella montagnei*. It gives all the reactions of montagnetol, but differs in having a lower melting point and a different crystal structure, and in being dextrorotatory. Hence it is identified as *d*-montagnetol. The higher melting compound is the racemic variety having no optical activity. The general results indicate that racemisation takes place even in the plant.

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CHEMOTHERAPY OF BACTERIAL INFECTIONS

Part VI. Synthesis of N^1-substituted Sulphanilamides: Poly- and Hetero-cyclic Derivatives

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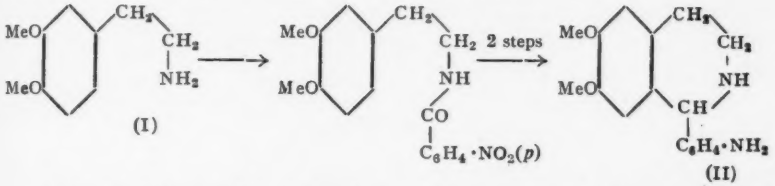
(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., F.A.SC., I.M.S.)

The studies on the therapeutic properties of various types of sulphanilamide derivatives in some experimental bacterial infections have convinced us that compounds with a higher degree or greater range of therapeutic activity than sulphanilamide should be searched for amongst its derivatives with cyclic, particularly heterocyclic, substituents at the sulphonamide radical. Since it is difficult at present to anticipate precisely the ring compound that will lead to the desired goal, systematic work has been undertaken to synthesise the above class of compounds with all feasible ring structures, so that we may not miss any with outstanding effects. In continuation of the work previously reported,[1] in this paper is described the synthesis of N^1-sulphanilamido derivatives of diphenylether, dibenzofuran, carbazole, acridine, chrysene, coumarin, tetrahydroisoquinoline and phenanthridine. In this preliminary study, only typical representatives of each ring system have been synthesised and if any of them show promise, further elaboration in that group will be made. The types of ring systems selected are such that they are either present in compounds showing significant pharmacological activity or expected to fill up the gaps in the data necessary to correlate chemical constitution with chemotherapeutic action.

All the compounds excepting 68 and 69 listed in the table were prepared by the customary method of condensing *para* acetaminobenzenesulphochloride with the corresponding cyclic amine and hydrolysing the resulting acetyl derivative to the free sulphanilamide derivative. The starting amines in most of the cases were prepared by methods recorded in the literature. In the experimental part, details are given in the case of those starting materials which are new or where better methods have been worked out. Thus, 4-aminodiphenylether[2] has been prepared by the hydrolysis of the N-acetyl derivative, in turn obtained by the Beckmann rearrangement of 4-phenoxyacetophenoneoxime.[3] A little known method[4] has been employed

for the preparation of dibenzofuran. 1-(*para* Amino-)phenyl-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxyisoquinoline (II) has been synthesised for the first time from 3 : 4-dimethoxyphenylethylamine (I) by the classical Bischler-Napieralsky reaction[5] through the obvious steps.



Amino sulphonamide derivatives of pyridine,[6] quinoline,[7] naphthalene,[9] and diphenyl[8] have been reported with no information on their therapeutic activity, excepting in the case of the naphthalene derivatives. Such compounds are of additional interest in ascertaining the implications of the Fildes-Woods theory [10, 11] of the mechanism of action of the sulphonamides.

No.	Name of Compound	Melting point °C.	Molecular formula	Percentage of Nitrogen	
				Found	Required
59	2-N¹-Sulphanilamidodiphenyether ..	149	$C_{18}H_{16}N_2O_3S$	7·9	8·2
	2-N¹-Acetsulphanilamidodiphenyether	162	$C_{20}H_{18}N_2O_4S$	7 6	7·3
60	4-N¹-Sulphanilamidodiphenyether ..	177–8	$C_{18}H_{16}N_2O_3S$	8·3	8·2
	4-N¹-Acetsulphanilamidodiphenylether	183	$C_{20}H_{18}N_2O_4S$	7·1	7·3
61	3-N¹-Sulphanilamidophenanthrene ..	213–5	$C_{20}H_{16}N_2O_2S$	7·8	8·1
	3-N¹-Acetsulphanilamidophenanthrene	244–5	$C_{22}H_{18}N_2O_3S$	6·9	7·1
62	6-N¹-Sulphanilamidochrysene ..	265	$C_{24}H_{16}N_2O_2S$	6·8	7·0
68	2-N¹-Sulphanilamidodibenzofuran[a] ..	242–3	$C_{18}H_{14}N_2O_3S$	..	..
64	3-N¹-Sulphanilamidocarbazole[b] ..	251 (dec.)	$C_{18}H_{15}N_3O_2S$	..	..
65	9-N¹-Sulphanilamidocarbazole ..	224 (dec.)	$C_{18}H_{15}N_3O_3S$	11·9	12·5
	9-N¹-Acetsulphanilamidocarbazole	202–3 (dec.)	$C_{20}H_{17}N_3O_3S$	10·5	11·1
66	6-N¹-Sulphanilamidocoumarin ..	189–90	$C_{15}H_{12}N_2O_4S$	8·7	8·9
67	9-N¹-Sulphanilamidoacridine dihydrochloride ..	..	$C_{19}H_{17}N_3O_2SCl_2$	9·6	10·0
	9-N¹-Acetsulphanilamidoacridine ..	273–5 (dec.)	$C_{21}H_{17}N_3O_3S$	10·5	10·8
70	1-(*p*-Sulphanilamido-) phenyl-1 : 2 : 3 : 4-tetra hydro-6:7-dimethoxyisoquinoline	162 (sint.) 159	$C_{23}H_{25}N_3O_4S$	9·4	9·6
71	9-(*m*-Sulphanilamido-) phenylphenanthridine	251–3 (dec.) (sint. 246)	$C_{25}H_{19}N_3O_2S$	9·4	9·9
68	2-Aminodiphenyl-(5?)-sulphonamide ..	186	$C_{12}H_{12}N_2O_2S$	10·6	11·0
69	4-Aminonaphthalenesulphonamide ..	250–1 (dec.)	$C_{10}H_{10}N_2O_2S$	12·0	12·6

(*a*) Described by Novelli[12] and given the m.p. 242–4° C.

(*b*) Described by Novelli[13] and given the m.p. 256–7° C.

(*c*) Described by Goldyrev and Postovskii[9] and given the m.p. 212° C.

Synthesis of some compounds of this type were therefore undertaken. 2-Acetaminodiphenyl on treatment with chlorosulphonic acid furnished a sulphochloride; this on treatment with ammonia followed by hydrolysis, yielded a product which by analogy has been described provisionally to be 2-amino-5-sulphonamidodiphenyl (compound 68). Under the conditions employed for the preparation of *para*-acetaminobenzenesulphochloride from acetanilide, the chlorosulphonation of 2-acetaminopyridine, 2-acetaminothiazole and 8-acetaminoquinoline were tried with no success, the starting products being recovered unchanged in all cases.

The compounds reported here are being tested in this Institute in experimental plague, β-hemolytic streptococcal and pneumococcal (type I) infections in mice and the results will be reported in due course.

Experimental

Synthesis of the Sulphanilamide derivatives (*all compounds except* 68 *and* 69).—The synthesis of these compounds being according to the well standardised methods, the details are omitted. The acetyl derivatives were obtained by condensing crystallised acetsulphanilylchloride with the corresponding amines in pyridine medium. Hydrolysis of the acetyl derivatives was carried out by means of 10% sodium hydroxide except in the cases of compounds 66, 67 and 70, where about 4-N-hydrochloric acid was used. The yields of the final products, except in the case of compound 70, were all good.

4-*Acetamidodiphenylether.*—A solution of *para* phenoxyacetophenone oxime (19·4 g.) in glacial acetic acid (130 c.c.) and acetic anhydride (100 c.c.) was saturated at 0° C. with dry hydrogen chloride by passing in a slow stream for 8 hrs. with occasional shaking, allowed to stand overnight and the separated acetyl derivative (15 g.) filtered; m.p. 130° C. (literature,[2] m.p. 127° C.).

4-*Aminodiphenylether hydrochloride.*—A mixture of the above amide (15 g.) and dil. hydrochloric acid (6 N, 200 c.c.) was boiled for 2 hrs. and the separated base hydrochloride filtered and washed with a little acetone; m.p. 225–27° C. (decomp.); (literature,[2] m.p. 222° C.).

Dibenzofuran.—A mixture of 2 : 2′-dihydroxydiphenyl (30 g.) and freshly fused zinc chloride (110 g.) were heated together at 230–50° during 4 hrs. and poured, while still warm, into dil. hydrochloric acid. The solid (m.p. 81–83° C., 25·2 g.) was filtered and thoroughly washed with dil. sodium hydroxide. A single distillation of this solid over sodium gave the pure dibenzofuran which crystallised from alcohol in colourless plates or needles; m.p. 83–84°; yield, 22 g.

(para *Nitro*)-*benzoylhomoveratrylamide.*—The amide which was prepared in good yield by the condensation of homoveratylamine and *para* nitrobenzoylchloride, separated from alcohol in faintly yellowish plates; m.p. 149°. (Found: N, 7·9; $C_{17}H_{18}O_5N_2$ requires N, 8·1%.)

1-(para *Nitro*)-*phenyl*-3 : 4-*dihydro*-6 : 7-*dimethoxyisoquinoline.*—A mixture of the above amide (crude, m.p. 143–45°, 8·7 g.) and phosphorous oxychloride (18 c.c.) was gently refluxed on sand-bath for 1½ hrs., cooled, decomposed with ice and worked up for a basic product. The dihydroisoquinoline derivative (crude, 7·8 g., m.p. 155–56°) separated from alcohol in silky needles; m.p. 158–9° C. (Found: N, 8·6; $C_{17}H_{16}O_4N_2$ requires N, 9·0%.)

1-(para *Amino*)-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*dimethoxyisoquinoline.*—The crude forementioned nitro product (6 g.), zinc dust (50 g.) and dil. sulphuric acid (500 c.c., 1 : 3) were heated on the boiling water-bath for 3 hrs. The mixture was filtered hot, and the residue thoroughly washed with hot water. The crude tetrahydro derivative (5·1 g., m.p. 150–52°) was obtained on basifying the solution. It separated from water in colourless needles; m.p. 151–53°. (Found: N, 9·4; $C_{17}H_{20}N_2O_2$ requires N, 9·9%.)

2-*Amino*-5 (?)-*sulphonamidodiphenyl.*—The crude sulphochloride prepared by treating 2-acetamidodiphenyl (11·5 g.) with chlorosulphonic acid (18 c.c.) and working up as usual, was added to liquor ammonia (175 c.c.) and ice (50 g.) with good stirring. After standing for about half an hour, it was filtered, the filtrate acidified and allowed to stand overnight. The crude acetyl derivative so obtained (4·2 g.), m.p. 195–98°, was hydrolysed by boiling with sodium hydroxide (2·5 N, 60 c.c.) for about an hour. The free amine obtained on neutralisation of the solution, crystallised from dil. alcohol in colourless plates; m.p. 185° after sintering at 183°; yield, 2·25 g.

We wish to express our grateful thanks to Lt.-Col. S. S. Sokhey, Director, Haffkine Institute, for his keen interest in this investigation and also to the Lady Tata Memorial Trust for the award of a Research Scholarship to one of us (S. R.). We also acknowledge gratefully a gift of coumarin from Prof. Dr. B. B. Dey.

Summary

With the object of studying the antibacterial effect of sulphanilamide derivatives with cyclic substituents at the sulphonamide radical, typical N^1-sulphanilamido derivatives of diphenylether, phenanthrene, chrysene, dibenzofuran, carbazole, coumarin, acridine, tetrahydroquinoline and phenanthridine have been synthesised and are reported. Aminosulphonamide derivatives of naphthalene and diphenyl are also described.

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SYNTHETIC EXPERIMENTS IN THE BENZO-PYRONE SERIES

Part V. Action of Aluminium Chloride on Karanjin

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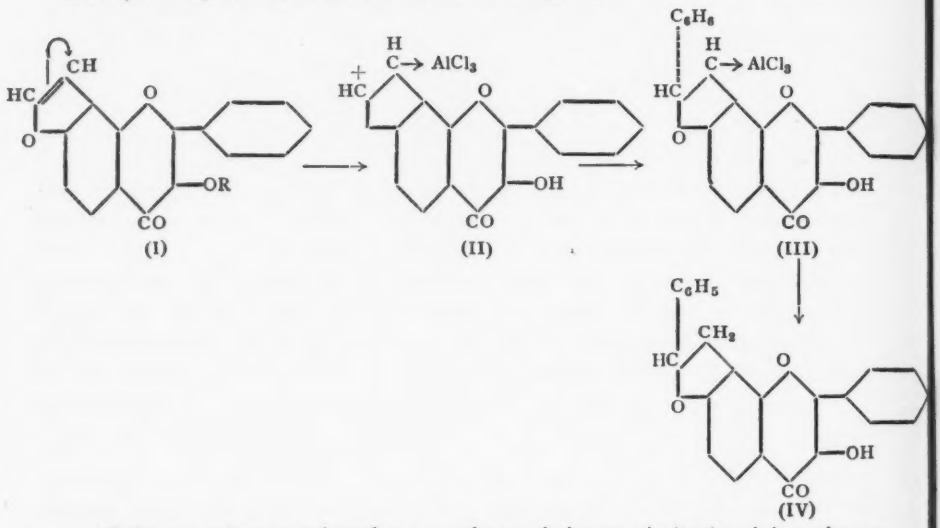
The constitution of karanjin which is one of the important crystalline compounds of pongamia oil has been established by a study of its reactions, an investigation of its decomposition products and by synthesis.[1] In the course of synthetic work on pyronofurans, the action of aluminium chloride on karanjin has been examined. If nitrobenzene is used as solvent, smooth demethylation takes place giving rise to a good yield of karanjonol (I, R = H). This hydroxy compound was originally obtained by Limaye from karanjin, by demethylation with hydrogen bromide.[2] Since benzene has been used by some investigators as solvent for demethylations and since it is much more convenient to work with, the reaction was studied in the presence of this solvent. In this case, however, instead of karanjonol an entirely new compound was obtained. From its properties and analysis, it was concluded that besides demethylation addition of benzene had taken place at the furan double-bond yielding α-phenyl-α: β-dihydro-karanjonol (IV). It forms a monoacetyl derivative. During methylation, the dihydrofuran ring seems to undergo partial opening, giving rise to a product which yields on analysis methoxyl values higher than that required for one methoxyl group.

That the furan double-bond is the one involved in the above condensation of karanjin was established by examining the behaviour of closely related flavones under the same conditions. For this purpose, 7-methoxy-flavone (V), 3-methoxy-7-hydroxy-flavone (VI) and 3:7-dimethoxy flavone (VII) were employed. In benzene solution smooth and complete demethylation took place in all the three cases and there was no addition of benzene. When, however, nitrobenzene was employed at about the same temperature, it was noticed that (V) was unaffected, (VI) underwent demethylation to yield 3:7-dihydroxy-flavone and (VII) suffered only partial demethylation yielding a monomethyl ether. The latter gave the reactions of a 3-hydroxy-flavone. Further, since 7-methoxy-flavone is unaffected in nitrobenzene solution, it is obvious that the new compound is 7-methoxy-3-hydroxyflavone. An easy method is thus available for the preparation of this compound which is otherwise not easily accessible. Our results further support the findings of Venkataraman and co-workers[3] that besides the methoxyl groups in

5 and 4′ positions, that present in 3 position of flavones is also susceptible to demethylation in nitrobenzene solution. The mild demethylating action of aluminium chloride in this solvent may be attributed to the formation of a co-ordination complex, $C_6H_5NO_2 \rightarrow AlCl_3$, which renders the reagent less easily available for the demethylation. This also explains the ready solubility of the reagent in the solvent.

In regard to the reaction of karanjin with benzene in the presence of aluminium chloride, the furan double-bond of the molecule obviously functions like an ethylenic double-bond and the addition is catalysed by aluminium chloride according to the following mechanism, the anionoid centre of benzene initiating the attack on the positive carbon atom of the aluminium chloride complex. Nitrobenzene is incapable of such nuclear activity owing to the existence of the nitro group.



Toluene, when employed as a solvent, behaves similarly giving rise to Tolyl-dihydro-karanjonol, which resembles very closely the phenyl derivative and yields similar acetoxy and methoxy derivatives.

Experimental

The general procedure adopted in regard to the demethylation of the methoxy flavones is described below with reference to 7-methoxy-flavone.

Action of aluminium chloride on 7-methoxy-flavone

(i) *In benzene solution.*—7-Methoxy-flavone (0·2 g.) was dissolved in benzene (10 c.c.), anhydrous aluminium chloride (Merck quality, 0·5 g.) added and the mixture refluxed on a water-bath (80–85°) for about

45 minutes, after which the benzene solution was decanted into another flask and evaporated to dryness. 5 c.c. of 1 : 1-hydrochloric acid was then added to each of the containers to decompose the aluminium chloride complex. The contents of the two flasks were filtered using the same filter and the solid recrystallised from acetic acid. Needle-shaped crystals melting at 239–40° were thus obtained. Mixed melting point with 7-hydroxy-flavone was undepressed (yield 0·15 g.).

(ii) *In nitrobenzene solution.*—The above experiment was repeated using nitrobenzene in the place of benzene. The solvent was finally removed by steam-distillation and the product recrystallised from alcohol. The starting material was recovered quite unchanged, in the form of rectangular plates melting at 110°.

On 7-hydroxy-3-methoxy-flavone

In this case both when benzene and nitrobenzene were employed as solvents, the final product was found to be the same. On recrystallisation from acetic acid, it was obtained as long and narrow rectangular plates melting at 257–58° (*cf.* 3 : 7-dihydroxy-flavone[4, 5] 258°).

On 3 : 7-dimethoxy-flavone

(i) *In benzene solution.*—0·3 g. of the dimethyl ether yielded finally 0·2 g. of 3 : 7-dihydroxy-flavone. The mixed melting point with the sample mentioned above was undepressed.

(ii) *In nitrobenzene solution.*—The procedure adopted was the same as for 7-methoxy-flavone. After removal of the solvent by steam-distillation, the precipitate in the flask was filtered and crystallised from glacial acetic acid. Yellow glistening plates melting at 177–78° were thus obtained in 75% yield. It gave a brown colour with ferric chloride and dissolved in sodium hydroxide to give a yellow solution (*cf.* 7-methoxy-flavonol[4] 180°).

Action of aluminium chloride on karanjin

(i) *In nitrobenzene solution—preparation of karanjonol.*—The reaction was carried out starting with karanjin (1 g.), nitrobenzene (20 c.c.) and aluminium chloride (2 g.). The final product was obtained, on crystallisation from glacial acetic acid, as stout rhombic prisms melting at 192–93°.

(ii) *In benzene solution—preparation of α-phenyl-α : β-dihydro-karanjonol.*—Karanjin (1 g.), benzene (15 c.c.) and aluminium chloride (2 g.) were used for the reaction. The final product was crystallised repeatedly from hot glacial acetic acid. 0·6 g. of a pale yellow compound crystallising in the form of short rectangular plates and melting at 260–62° was obtained. It gave a brownish violet colour with ferric chloride. (Found : C, 77·1; H, 4·9 and there was no loss on drying at 120° for 2 hours. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%.)

The above compound (0·2 g.) was acetylated with anhydrous sodium acetate and acetic anhydride. The acetyl derivative came down from alcohol as thin rectangular plates melting at 138–39°. (Found: C, 75·2; H, 4·8; $C_{25}H_{18}O_5$ (monoacetyl derivative) requires C, 75·5; H, 4·5%.)

The methyl ether obtained by methylation with dimethyl sulphate and sodium hydroxide, crystallised out from alcohol in rectangular plates melting at 151–53°. (Found: OCH_3, 13·5; $C_{23}H_{15}O_3$ (OCH_3) requires OCH_3, 8·4; $C_{23}H_{14}O_2$ (OCH_3)$_2$ requires OCH_3, 16·2%.)

(iii) *In toluene solution—preparation of α-tolyl-α: β-dihydro-karanjonol.*—The method of preparation was just similar to the above except that in the place of benzene, toluene was used and finally the toluene was removed by steam-distillation. The product was crystallised from hot glacial acetic acid. Broad rectangular plates were thus obtained and the substance melted at 274–76°. The colour with ferric chloride was similar to that given by the benzene compound. (Found: C, 77·2; H, 5·2 and there was no loss on drying at 110–20° for 2 hours. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%.)

The acetyl derivative was obtained in rectangular plates when crystallised from alcohol. It melted at 145–46°. (Found: C, 75·9; H, 5·4; $C_{26}H_{20}O_5$ (monoacetyl derivative) requires C, 75·7; H, 4·9%.)

The methyl ether crystallised from alcohol as short plates melting at 157–59°. (Found: OCH_3, 11·6; $C_{24}H_{17}O_3$ (OCH_3) requires OCH_3, 8·1; $C_{24}H_{16}O_2$ (OCH_3)$_2$ requires OCH_3, 15·6%.)

Summary

By the action of aluminium chloride on karanjin using nitrobenzene as solvent, smooth conversion into karanjonol could be effected. When benzene is used instead, besides demethylation a molecule of benzene adds on to yield α-phenyl-α: β-dihydro-karanjonol. Similar addition takes place in the case of toluene also. That the double-bond of the furan ring is involved in this reaction has been established by studying the behaviour of a few similar flavone compounds under the same conditions. It has been incidentally shown that a methyl ether group in the 3-position is readily affected in nitrobenzene solution whereas in the 7-position it is stable and the preparation of 7-methoxy-flavonol is easily carried out by demethylation of 3: 7-dimethoxy-flavone.

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PECHMANN CONDENSATION OF PHENOLS WITH ETHYL BUTYROACETATE

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In continuation of the previous work[1] to study the reactivity of γ-substituted acetoacetic esters in the Pechmann reaction, the reactivity of ethyl butyroacetate which is ethyl γ-ethyl aceto-acetate and which was prepared by the method of Bongert[2] has now been studied.

It has been found that ethyl butyroacetate condenses with resorcinol, orcinol, pyrogallol, phloroglucinol and α-naphthol in presence of sulphuric acid to give 4-propyl coumarin derivatives. The coumarin structure of the compounds was proved by the preparation of the cinnamic acid derivatives.

Phenol, β-naphthol, quinol, *m*-cresol, methyl β-resorcylate and resacetophenone did not condense with ethyl butyroacetate either in the presence of sulphuric acid or in the presence of phosphoryl chloride, phosphorous pentoxide and anhydrous aluminium chloride.

The results show that a γ-ethyl substituent in ethyl acetoacetate has considerable inhibiting effect on the course of the Pechmann reaction, for, phenol, *m*-cresol, quinol and methyl β-resorcylate which do not condense with ethyl butyroacetate do condense with ethyl acetoacetate to give coumarins in presence of sulphuric acid as found by previous workers.[3, 4, 5, 6] Further, the inhibiting effect of the γ-ethyl substituent in ethyl acetoacetate is greater than that of the α-ethyl substituent for it has been found that ethyl α-ethyl acetoacetate condenses with *m*-cresol and methyl β-resorcylate.[4, 7] The γ-ethyl substituent also seems to have a greater retarding effect than a negative substituent like the carbethoxy because ethyl acetone dicarboxylate which may be considered as ethyl γ-carbethoxy acetoacetate condenses with *m*-cresol and quinol[8] and also with methyl β-resorcylate.[9]

Experimental

7-Hydroxy-4-propyl coumarin.—To a mixture of ethyl butyroacetate (2·0 g.) and resorcinol (1·3 g.), sulphuric acid (75%, 15 c.c.) was slowly added. The reaction mixture was allowed to stand overnight and then poured in

powdered ice. The yellow solid (0·5 g.) obtained was crystallised from alcohol in needles, m.p. 130°. It gave blue fluorescence with alkali. (Found: C, 70·1; H, 5·8; $C_{12}H_{12}O_3$ requires C, 70·5, H, 5·8 per cent.)

The acetyl derivative.—7-Hydroxy-4-propyl coumarin (0·5 g.) was refluxed on a wire-gauze for 4 hours with anhydrous sodium acetate (1·0 g.) and acetic anhydride (5 c.c.). The product obtained on adding the reaction mixture to water was crystallized from rectified spirit in tiny needles, m.p. 118-19°. (Found: C, 68·1, H, 5·3; $C_{14}H_{14}O_4$ requires C, 68·3, H, 5·6 per cent.)

The methyl ether.—7-Hydroxy-4-propyl coumarin (0·5 g.) was dissolved in acetone (50 c.c.) and refluxed for twenty hours with fused potassium carbonate (1·0 g.) and methyl iodide (5 c.c.). The acetone was removed by evaporation and water was added. The product obtained was crystalised from very dilute alcohol in tiny shining needles, m.p. 145–46°. (Found: C, 71·3, H, 6·4; $C_{13}H_{14}O_3$ requires C, 71·5, H, 6·4 per cent.)

2 : 4-*dimethoxy β-propyl cinnamic acid.*—7-Hydroxy-4-propyl coumarin (1 g.) was dissolved in acetone, dimethyl sulphate (8 c.c.) was added and the reaction mixture heated on a boiling water-bath for 8 to 10 minutes. Sodium hydroxide (5%, 30 c.c.) was then added gradually with constant shaking, the heating being carried on all the time. More dimethyl sulphate (10 c.c.) and sodium hydroxide (40 c.c.) were added alternately with shaking. Finally, excess of sodium hydroxide was added and heating continued for about half an hour. It was then left overnight. Next day the solution was filtered and acidified with con. HCl. It was then kept in the frigidaire and on the next day the solid obtained was filtered, washed and treated with sodium bicarbonate solution. The product obtained on acidification of the sodium bicarbonate solution was crystallized from dilute alcohol in tiny shining silky needles, m.p. 83-85°. It decolourizes bromine water and dilute potassium permanganate solution. It dissolves in sodium bicarbonate solution with effervescence. (Found: C, 67·0, H, 7·0; $C_{14}H_{18}O_4$ requires C, 67·2, H, 7·1 per cent.)

5-*Hydroxy*-4-*propyl*-7-*methyl coumarin.*—Prepared from orcinol (1·6 g.), ethyl butyroacetate (2 g.) and sulphuric acid (75%, 15 c.c.) as usual, was crystallized from alcohol in needles, m.p. 180°. It gave deep yellow colouration with sodium hydroxide. (Found: C, 72·1, H, 6·1; $C_{13}H_{14}O_3$ requires C, 71·7, H, 6·4 per cent.)

The acetyl derivative.—Prepared as before was crystallised from rectified spirit in tiny needles, m.p. 120–21°. (Found: C, 69·4, H, 6·1; $C_{15}H_{16}O_4$ requires C, 69·25, H, 6·25 per cent.)

The methyl ether.—Prepared as before, was crystallised from very dilute alcohol in tiny shining needles, m.p. 78–79°. (Found: C, 72·3, H, 6·8; $C_{14}H_{16}O_3$ requires C, 72·4, H, 6·9 per cent.)

2 : 6-*Dimethoxy*-4-*methyl*-β-*propyl cinnamic acid.*—Prepared as before, was crystallised from water with a few drops of alcohol in tiny fine silky needles, m.p. 165°. (Found: C, 68·3, H, 7·2; $C_{15}H_{20}O_4$ requires C, 68·2, H, 7·5 per cent.)

7 : 8-*Dihydroxy*-4-*propyl coumarin.*—Prepared from pyrogallol (1·6 g.), ethyl butyroacetate (2·0 g.) and sulphuric acid (75%, 15 c.c.); was crystallised from alcohol in needles, m.p. 198–200°. (Found: C, 65·8, H, 5·2, $C_{12}H_{12}O_4$ requires C, 65·5, H, 5·5 per cent.)

The diacetyl derivative.—Prepared as usual was crystallised from dilute alcohol in tiny needles, m.p. 150–52°. (Found: C, 62·8, H, 5·4; $C_{16}H_{16}O_6$ requires C, 63·1, H, 5·3 per cent.)

The dimethyl ether.—Prepared as usual, was crystallised from dilute alcohol in tiny shining needles, m.p. 95°. (Found: C, 67·9, H, 6·2; $C_{14}H_{16}O_4$ requires C, 67·8, H, 6·4 per cent.)

2 : 3-4-*Trimethoxy*-β-*propyl cinnamic acid.*—Prepared as usual was crystallised from aqueous alcoholic solution in fine silky needles, m.p. 134-36°. (Found: C, 64·4, H, 7·1; $C_{15}H_{20}O_5$ requires C, 64·4, H, 7·1 per cent.)

5:7-*Dihydroxy*-4-*propyl coumarin.*—Prepared from phloroglucinol (2 g.), ethyl butyroacetate (2 g.) and sulphuric acid (75%, 15 c.c.) was crystallised from alcohol in needles, m. p. 258°. (Found: C, 64·9; H, 5·2; $C_{12}H_{12}O_4$ requires C, 65·4, H, 5·4 per cent.)

The diacetyl derivative.—Prepared as usual was crystallised from rectified spirit in tiny needles, m.p. 145°. (Found: C, 62·8, H, 4·9; $C_{16}H_{16}O_6$ requires C, 63·1; H, 5·2 per cent.)

The dimethyl ether.—Prepared as usual was crystallised from dilute alcohol in needles, m.p. 150°. (Found: C, 67·6, H, 6·2; $C_{14}H_{16}O_4$ requires C, 67·8, H, 6·4 per cent.)

2 : 4 : 6-*Trimethoxy*-β-*propyl cinnamic acid.*—Prepared as usual was crystallised from water with a little alcohol in fine silky needles, m.p. 140°. (Found: C, 64·4, H, 7·2; $C_{15}H_{20}O_5$ requires C, 64·4, H, 7·1 per cent.)

α-*Naphtha* 4-*propyl* α-*pyrone.*—Prepared from α-naphthol (1·9 g.), ethyl butyroacetate (2 g.) and sulphuric acid (75%, 15 c.c.) was crystallised from alcohol (charcoal) in needles, m.p. 108–10°. (Found: C, 79·9, H, 5·8; $C_{16}H_{14}O_2$ requires C, 80·4, H, 5·8 per cent.)

Attempts to prepare the cinnamic acid derivative from this product by the usual method were unsuccessful.

Our thanks are due to Dr. J. V. Lakhani and Dr. R. C. Shah for their kind interest and suggestions during the course of the work.

Summary

Ethyl butyroacetate has been found to condense with resorcinol, orcinol, pyrogallol, phloroglucinol and α-naphthol in presence of sulphuric acid to give 4-propyl coumarin derivatives. Phenol, *m*-cresol, quinol, β-naphthol, methyl β-resorcylate and resacetophenone however did not condense either in presence of sulphuric acid or in presence of phosphorous pentoxide, phosphoryl chloride or anhydrous aluminium chloride as condensing agents.

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VISCOSITY MEASUREMENTS DURING THE COAGULATION AND GELATION OF CONCENTRATED SOLS OF ZIRCONIUM AND STANNIC HYDROXIDES

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Most of the early studies in gels were confined to gels of organic substances. This was probably because they can be easily prepared in a transparent or translucent state and many of them are heat reversible. During recent years a large number of gels of inorganic substances have been prepared in as transparent a condition as the organic gels[1] and some of them have been shown to exhibit the phenomena of reversible isothermal sol-gel transformation and thixotropic behaviour. These inorganic gels have been prepared by either of the three following methods:—

(1) by metathetical reactions,

(2) by the addition of electrolytes to a suitably dialysed sol,

(3) by diluting a true solution of the gel-forming substance in a suitable solvent.

It appears from the above that the first requisite for the formation of gels is that the gel-forming substance should be obtained in a sol condition. This takes place in the first method, in some cases, by the condensation of the molecules of the substance and, in others, by the peptisation of its precipitate by ionic adsorption and mechanical action. In the third method the gel-forming substance being less soluble in the diluted medium, goes over to the sol condition due to the condensation of molecules.

The second necessary condition seems to be that the density of charge on the particles of the sol should be low and that the sol should undergo coagulation in some way. These necessities are evidenced by the facts that (i) gels have been prepared by the second method mentioned above and (ii) they are sometimes observed to form in the dialysing bag when a suitable sol is extremely dialysed.

The third and rather important condition for the formation of gels is that the concentration of the gel-forming substance should be reasonably large. The necessity of this condition has been pointed out by Weiser and

Bradford[2] who conclude that the supersaturation of the gel-forming substance should be very high. Von Wiemarn[3] has found that a gel is formed only when the value of N, the form coefficient of the precipitate, given by the relation

$$N = V\frac{P}{L}$$

(where V is a function of the viscosity of the reaction system, P the excess of the concentration of the substance to be precipitated and L its solubility), is very great. Further, various investigators[4] have experimentally shown that no gel is formed by the first method if the concentrations of the gel-forming solutions are not suitably chosen. Also no gel will be formed by the second method if the sol is not fairly concentrated. These conclusions are also supported by the theory suggested by Bogue[5] and accepted in principle by McBain and co-workers,[6] Barrat,[7] and Krishnamurti.[8] According to this theory a gel is formed only when a large number of fibrils of which it is composed and which are in a highly hydrated state, cohere in a small volume.

The discussion set forth above leads to the conclusion that gelation consists in (i) the coagulation of the concentrated sols of the gel-forming substance, the particles of which do not carry a high density of charge and (ii) the subsequent formation of specific structures. The process of gelation should, therefore, be akin to the coagulation of concentrated sols. De Jong[9] concludes from his experiments that the gelation of agar sol has all the characteristics of flocculation.

In the present investigation an attempt has been made to examine the relationship between the processes of coagulation and gelation of systems which contain the same coagulating and gelating substance. For this purpose sols and gels of zirconium hydroxides were first studied and later, experiments were performed with sols of stannic hydroxide since they, under not very different conditions, were found to give rise to true coagulation and gelation.

Processes of coagulation and gelation have been studied by several workers by various methods, such as those involving the measurements of viscosity, the optical properties (refractive index, extinction coefficient, scattering of light, transparency or opacity) and others. For the purpose of this investigation the viscosity method was employed and the results obtained are given in the following pages.

Experimental

Experimental method employed in the study of viscosity has been described by Prasad and Modak.[10] The length and the diameter of the capillary

of the viscometer were 6·40 cm. and 0·062 cm. respectively. The constant of the apparatus determined by using 60 per cent. solution of sucrose was found to be 0·00218.

(*a*) *Coagulation of zirconium hydroxide sol.*—Zirconium hydroxide sol was prepared in the same manner as described by Prasad and Modak[11] and its concentration was also the same, *i.e.*, 0·06042 moles of zirconium oxide per litre.

3 c.c. of the sol were drawn out with a clean pipette into a clean dry test tube and a known volume of the solution of the electrolyte was taken into another clean dry test-tube. To each of these test tubes sufficient amount of twice-distilled water was added to make up the volume in each of the test tubes to 5 c.c. These were then corked and kept in the thermostat for 35 minutes during which period they attained the temperature of the thermostat. The maximum error in the adjustment of the thermostat never exceeded $\pm 0{\cdot}02°$. The two solutions were then mixed by pouring the contents of one test tube into the other; this was repeated four times. To make this process of mixing as uniform as possible the test tube containing the mixture was just resting on the other while pouring, and the actual pouring was done fairly slowly.

Viscosity readings were continued until particles were visible in the coagulating system. As a rule, this happened suddenly and immediately the separation of the liquid and solid portions into two layers could be detected in the viscometer. When this condition was reached, the readings were either very low or could not be taken at all since the particles formed obstructed the capillary.

Results obtained are shown graphically in which the viscosity (expressed in millipoises) has been plotted against the average time (expressed in minutes) after the mixing of the sol and the electrolyte solution, at which the viscosity readings were taken. Fig. 1 gives the changes in viscosity during the coagulation of the sol on the addition of various volumes of 2·5 N-KCl solution at 33°.

(*b*) *Gelation of zirconium hydroxide gels.*—Gels of zirconium hydroxide were prepared by the method of Prakash.[12] Solutions of sodium acetate and zirconium nitrate of the same concentrations as employed by Prasad and Modak (*loc. cit.*) were used. The gels prepared as above presented considerable difficulty in the measurement of viscosity. In the first instance these gels became very stiff during the course of setting and secondly some bubbles appeared in the capillary tube during the rise and fall of the gel-forming mixture. The result obtained with a mixture containing

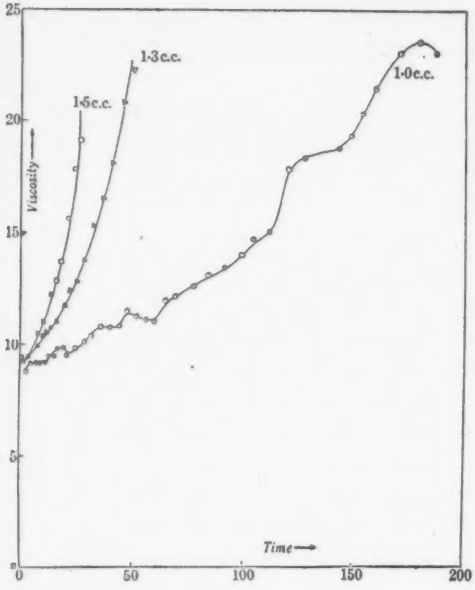

FIG. 1

Zirconium hydroxide sol
Coagulator KCl (2·5 N)
Temperature 33°

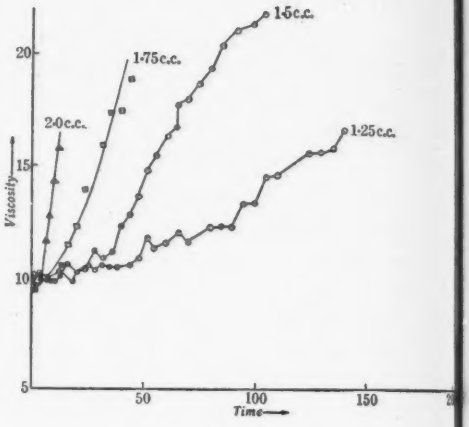

FIG. 3

Coagulator KCl (2·5 N)
(Stannic hydroxide undialysed sol)

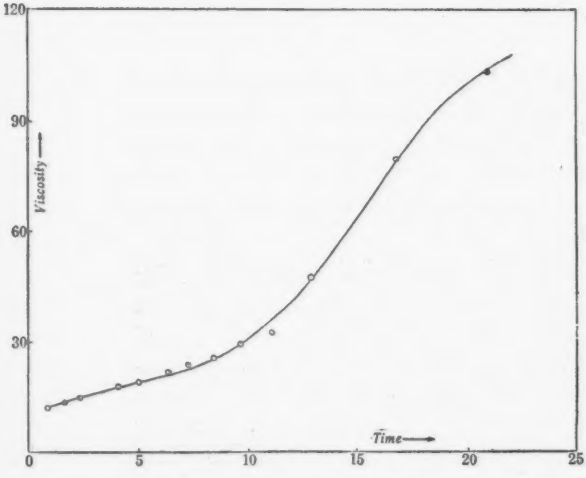

FIG. 2

Zirconium hydroxide gel
Temperature 33°

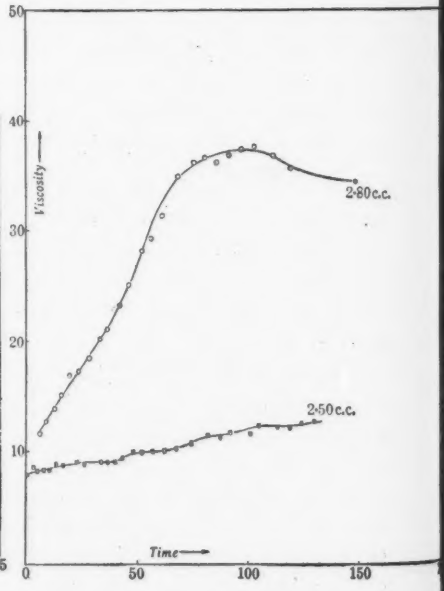

FIG. 4

Stannic hydroxide sol (undialysed)
Coagulator $HgCl_2$ (0·037 N)
Temperature 33°

4·86 c.c. of zirconium nitrate solution (10%) diluted to 5 c.c. and 1·62 c.c. of sodium acetate solution (3·84 N) also diluted to 5·0 c.c. is shown in Fig. 2.

(*c*) *Coagulation of stannic hydroxide sol.*—The sol was prepared in the same manner as described by Prasad and Modak (*loc. cit.*) and the concentration of the sol was also the same (SnO_2 content = 0·4725 moles, per litre). The viscosity measurements were made with undialysed sol and the sol dialysed for 12 days. Water outside the dialysing bag was changed twice and sometimes thrice a day and was always maintained at the same level as that of the sol in the bag.

4·0 c.c. of the sol were taken out in a clean test tube and 1·0 c.c. of distilled water was added to it. In another test tube a known volume of the electrolyte solution was taken and it was suitably diluted to make up the volume to 5·0 c.c. The rest of the procedure was the same as described before.

Figs. 3 and 4 give the various changes with time on the addition of different volumes of 2·5 N-KCl and 0·037 N-$HgCl_2$ solutions, respectively, at 33°, to the undialysed sol.

Figs. 5 and 6 give the results obtained with sol dialysed for 12 days, under the same conditions as given above. The coagulating mixture was observed to become very viscous when 0·60 c.c. and 0·80 c.c. of the $HgCl_2$ solution were added to the sol, and on standing for a long time the coagulum separated out but the mixture never set to a gel.

(*d*) *Gelation of stannic hydroxide sol.*—It has been found by Dhar and Varadanam[13] that the stannic hydroxide sol prepared as described above sets to a jelly on continued dialysis. A transparent jelly of stannic hydroxide is also formed when its concentrated sol is treated with a solution of hydrochloric acid or of potassium and barium chloride. The gels obtained by them showed thixotropic behaviour.

The sol of stannic hydroxide prepared for the coagulation experiments was allowed to dialyse till practically no electrolytes passed out during dialysis. This sol was stored in a Jena glass flask and was used for all the experiments. On the addition of electrolytes to this sample, no coagulation was observed and the whole mixture set to a clear thixotropic gel after sometime.

5 c.c. of the sol were taken in one test tube and different volumes of solutions of electrolytes were made up to 5 c.c. in the other test tube and the two were mixed in the usual manner afterthey had attained the temperature of the thermostat. The viscosity readings of the gel-forming system were

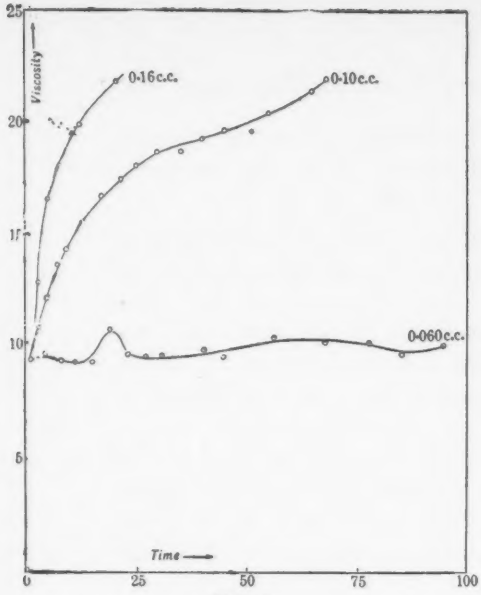

FIG. 5

Coagulator KCl (2·5 N)
Temperature 33°
(12 days dialysed sol)
$Sn(OH)_4$ sol

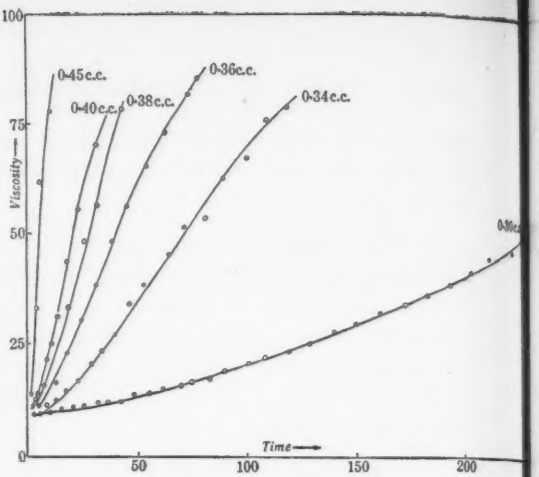

FIG. 7

Extremely dialysed sol
Coagulator KCl (·5 N)
Temperature 33°
$Sn(OH)_4$ sol

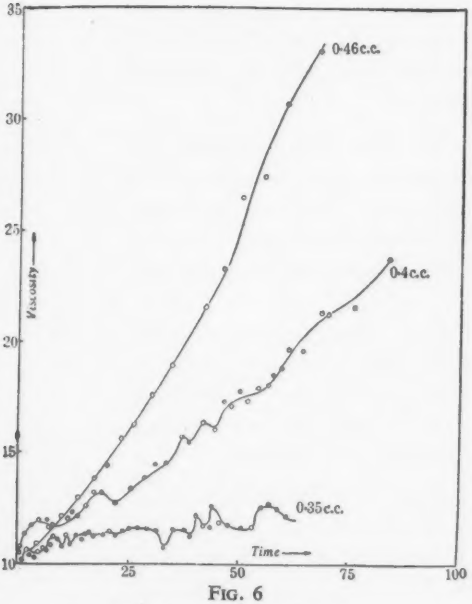

FIG. 6

Coagulator $HgCl_2$ (0·037 N)
Temperature 33°
(12 days dialysed sol)
$Sn(OH)_4$ sol.

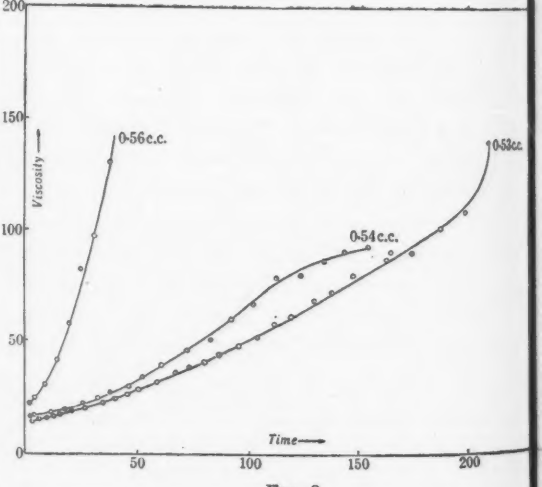

FIG. 8

Coagulator $BaCl_2$ (0·031 N)
Temperature 33°
Highly dialysed $Sn(OH)_4$ sol

taken in the manner described above and they were continued till the viscosity increased so high that the time of rise and fall of the mixturein the viscometer was sufficiently long.

Figs. 7, 8 and 9 give the results obtained on the addition of different volumes of 0·5 N-KCl, 0·031 N-$BaCl_2$ and 0·018 N-$HgCl_2$, respectively, at 33°.

Discussion and Results

The addition of electrolytes to the zirconium hydroxide sol and the sol of stannic hydroxide undialysed or dialysed for 12 days produces coagulation. A gel is formed, on the other hand, by the addition of coagulators, to the extremely dialysed stannic hydroxide sol.

It would be observed that the curves in Figs. 1 and 3 show a common behaviour in the sense that whereas some curves rise continuously and smoothly, a few represent an ' S ' shape comprised of zones[14]. This is markedly observed in the case of the curves for 1·0 c.c. in Fig. 1 and of those for 1·25 c.c. and 1·50 c.c. in Fig. 3. Generally an increase in the concentration of the coagulator appears to remove the zones (*cf.* curves for 1·25 c.c., 1·65 c.c. and 2·0 c.c. in Fig. 3; 1·0 c.c., 1·3 c.c. and 1·5 c.c. in Fig. 1). Joshi and Nanjappa noticed larger changes in the viscosity values during the coagulation of ferric hydroxide sol than those shown in Figs. 1 and 3. The smaller changes in the present case may be due to the fact that fairly concentrated sols have been used and this may have caused increased autocatalytic effect of coagulation under these conditions. An interesting point in the curve for 2·0 c.c. in Fig. 3, is the initial decrease in viscosity before it tends to rise rapidly in a smooth manner, a fact observed by Joshi and co-workers in several cases of slow coagulation.

The coagulation of the same sol (undialysed stannic hydroxide sol) by mercuric chloride, Fig. 4, does not show the same characteristics as observed during its coagulation by KCl (*cf.* Fig. 3). The viscosity curve in the presence of 2·5 c.c. is a very slow rising one and the zones are not very significant. On increasing the amount of the electrolyte to 2·8 c.c. the curve becomes a rapidly rising one. It appears that the changes in viscosity at any given interval of time are not commensurate with the amount of the electrolyte added.

The dialysis of the stannic hydroxide sol for 12 days changes its condition to a very great extent. This effect can be seen best by comparing the coagulation curves for the dialysed sol by KCl and $HgCl_2$, Figs. 5 and 6, respectively, with those for the undialysed sol in Figs. 3 and 4. The curve with 0·35 c.c. in Fig. 6 is a zonal one and does not show large total changes in viscosities.

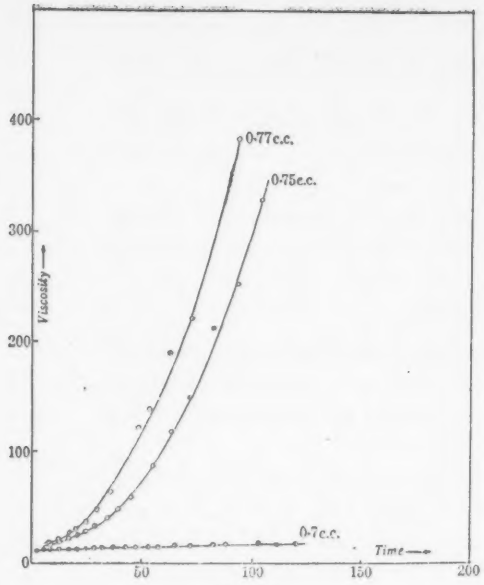

FIG. 9

Coagulator $HgCl_2$ (0·018 N)
Temperature 33°
Highly dialysed $Sn(OH)_4$ sol

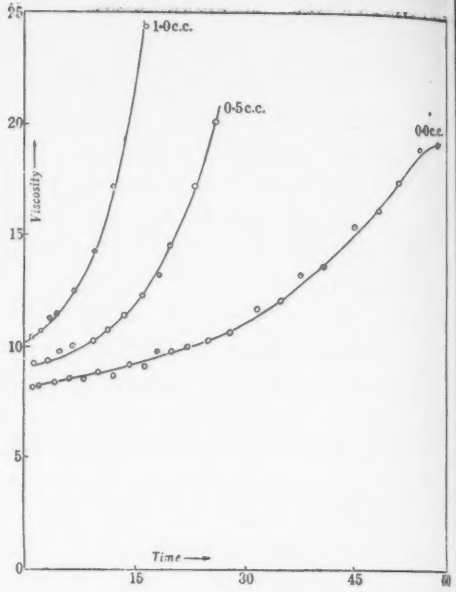

FIG. 11

Effect of alcohol
Temperature 43°

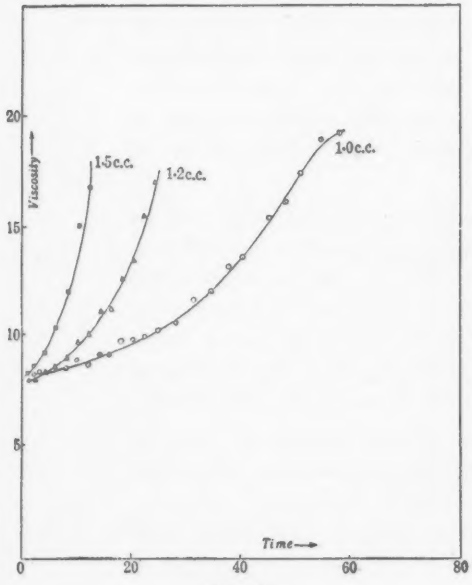

FIG. 10

Zirconium hydroxide sol
Coagulator KCl
Temperature 43°

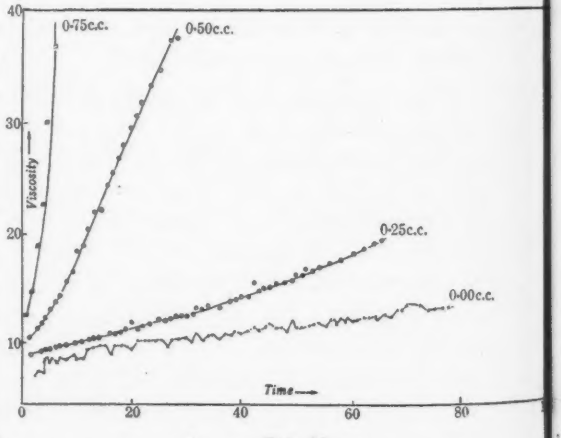

FIG. 12

Effect of alcohol on gelation by $HgCl_2$
Temperature 43°
(28 c.c. of 0·037 N)
Highly dialysed $Sn(OH)_4$ sol

It appears necessary to make a distinction between two types of viscosity-time curves indicative of rapid coagulation. The type of curve indicated by 0·46 c.c. of $HgCl_2$ solution in Fig. 6 seems to be obtained if the rate of coagulation indicated by the viscosity-time curves is comparatively slow. Curves of this type have previously been obtained by various workers using the viscosity and the transparency methods.[15] If, however, the coagulation is very rapid, the curve is of the type obtained with 0·16 c.c. of KCl shown in Fig. 5. Such curves too have been obtained by a number of workers by using the above-mentioned methods.[16] These types of curves could probably have been obtained with the sol dialysed for 12 days by using concentrations of $HgCl_2$ higher than 0·60 c.c. or 0·80 c.c. Attempts made in this direction showed that no curves could be obtained easily for these amounts of the coagulator but an observation was made that the whole mixture sets very rapidly.

It was observed that the zones observed with zirconium hydroxide sol in the presence of 1·0 c.c. of the coagulator at 33°, disappear when the temperature is raised to 43°. The viscosity-time curves for other mixtures of the coagulator and the zirconium hydroxide sols also undergo a change in magnitude but not in their characteristics. This effect has been brought out in curves shown in Fig. 10. The effect of temperature on the coagulation of zirconium hydroxide sol would thus appear to hasten the process of coagulation, carrying it from the slow region to the rapid one. A rise in temperature by 10° reduces the total time of coagulation to nearly $\frac{1}{3}$ of that at the lower temperature and the curve for 1·3 c.c. of sol at 33° corresponds fairly well to that for 1·0 c.c. at 43°.

Similar effect is observed when methyl or ethyl alcohol is added to the coagulating sol. The addition of 0·5 c.c. and 1·00 c.c. of ethyl alcohol to the zirconium hydroxide sol coagulated by 1·5 c.c. of KCl at 33° and 43° and the addition of the same amounts of methyl and ethyl alcohols to the stannic hydroxide sol (dialysed for 12 days) coagulated by 0·43 c.c. of 0·037 N-$HgCl_2$ showed a shortening of the coagulation period and the removal of any irregularities. The 'S' shape nature of the curves changes to that corresponding to rapidly rising ones and the reduction in the period of coagulation is fairly proportional to the original coagulation time. Two such curves representative of this effect are shown in Fig. 11. The effect of the higher alcohol seems to be greater than that of the lower ones.

Viscosity-time curves obtained with the extremely dialysed sol in the presence of potassium, barium and mercuric chlorides are shown in Figs. 7, 8 and 9. In the presence of potassium chloride in smaller concentrations these

curves are ' S ' shaped but become rapidly rising ones when larger amounts are used. The addition of $BaCl_2$ yields the same type of results. Mercuric chloride shows a different behaviour. The curves obtained in the presence of 0·77 c.c. and 0·75 c.c. are rapidly rising ones and they change over to an almost flat curve showing practically no viscosity changes, when 0·70 c.c. of $HgCl_2$ are used. Similar behaviour of $HgCl_2$ is seen from curves in Fig. 4. The curves for viscosity changes during the gelation of stannic hydroxide sol show no indications of any zonal effect during gelation. On the whole, the curves for gelation correspond to the first type of rapid coagulation referred to above.

As has been already stated in the beginning highly dialysed sol of stannic hydroxide produced gels on the addition of electrolytes. However, the addition of a little NH_4OH produced no gelation but effected a very slow coagulation. Since the stannic hydroxide sol is negatively charged, it is shown from the above that the tendency of stannic hydroxide sol to give rise to coagulation or gelation depends on the concentration of the hydroxyl ions adsorbed by the micelles.

The viscosity-time curve obtained from another sample of extremely dialysed stannic hydroxide sol prepared in a similar manner as described above and coagulated by 0·28 c.c. of 0·037 N-$HgCl_2$ is shown in Fig. 12. The effect of the addition of different amounts of ethyl alcohol on the same gelating mixture is also shown in this figure. These curves show that under the conditions stated above the course of gelation of stannic hydroxide gels is zonal and these zones disappear on the addition of alcohol.

The curve for the viscosity changes in zirconium hydroxide gel obtained at temperature 33° is shown in Fig. 2. The curve is precisely ' S ' shaped and is similar to the ones obtained during the coagulation of a sol. This nature of the curves was also observed with other mixtures which could not be studied upto the gelation point due to reasons stated before. It shows the usual characteristics of a slow increase in the first and a rapid one in the latter stages. The method of preparation of this gel is evidently different from that of the stannic hydroxide sol.

It would appear from the foregoing conclusions that the curves for the coagulation and the gelation of the same sol show similar characteristics. Though coagulation is the first step in the complex process of gelation, the main characteristics of coagulation seem to dominate the total changes brought about during the gelation process leading upto the formation of a definite structure. While it cannot be visualised that the processes latter to the coagulation of the gelating substances are not different from the former, it is certain

that the viscosity as a property fails to show the changes occurring at this stage. Opacity measurements carried out by Prasad and Modak (*loc. cit.*) have also yielded results which indicate a similarity in the coagulation and gelation processes. Thus it appears that both viscosity and opacity measurements have also their limitations in the study of colloids and their behaviour. It is possible that some property of colloids other than those employed so far may reveal the inner characteristics of the gelation process taking place subsequent to coagulation stage.

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APPLICATION OF POTASSIUM FERRICYANIDE METHOD FOR THE ESTIMATION OF CARBOHYDRATE IN CANE LEAVES

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1. Introduction

THE permanganate method of Bertrand (1923) and the iodine sulphate method of Schaffer and Hartmann (1921) for the estimation of carbohydrate in leaves are widely accepted. The principle underlying both these methods consists in the reduction of copper sulphate solution in the presence of weak alkalis the reduced copper being measured from the titration values of N/20 $KMnO_4$ or N/10 $Na_2S_2O_3$ solution. The permanganate method claims superiority due to its applicability to highly coloured solutions which often interfere with the end-point of the iodine titration although the authors during the course of their work experienced considerable difficulty in accurately defining the neutral point even in this case. Neither of the two methods, however, gives direct values for glucose, they being read from the graphs drawn with N/20 $KMnO_4$ or N/10 $Na_2S_2O_3$ solutions against mgms. of glucose, so that results obtained therefrom cannot always represent the true values. In addition the methods are time consuming, laborious and costly. Thus a method that would enable the direct estimation of glucose besides being simpler, less laborious and more economical is a desideratum.

Attempts were, therefore, made to see if the potassium ferricyanide method so succesfully used by the authors (1938) in cane juice analysis could be equally successfully employed in the estimation of glucose in cane leaves and the results obtained from experiments during the last crushing season have amply shown that this latter method besides being simpler, quicker and more economical gives excellent comparable results with the standard methods while as regards precision it is decidedly superior.

2. Experimental Procedure

Method of extraction of carbohydrates in leaves is similar in all the three methods and largely follows the standard procedure namely that 10·0 gm. of sampled cane leaves are treated with 150 c.c. of boiling alcohol, the solution decanted and the plant materials are washed out with 85% alcohol into a soxhlet extractor fitted into a 250 c.c. flask three-fourth full of alcohol (with a spatula tip full of $CaCO_3$ in it). The extracter is then fitted to a condenser and the whole apparatus heated on a water-bath

for 5–6 hours. The alcohol is poured off through filter-paper into a 500 c.c. flask, the filter-paper being washed with 85% alcohol and to this is added the original decanted extract. This filtrate is cooled, made up to volume, shaken well and 50 c.c. taken out for the estimation of alcoholic soluble matter. This alcoholic extract (450 c.c. or 500 c.c. in case no solution is taken for the estimation of alcoholic soluble matter) is now heated in a vaccum flask on a water-bath at 50–55° C. and the distillation is continued until only 15 c.c. approximately of the extract remains. This residue is then washed into a beaker with hot water and 20 c.c. of saturated solution of neutral lead-acetate added and the beaker allowed to stand for an hour when it is filtered into another 500 c.c. beaker, the bottom of which is covered with potassium oxalate crystals. Lead oxalate precipitates out and the washings are continued till about 400 c.c. of the filtrate is collected in the beaker. This is allowed to stand overnight, when lead oxalate is filtered off, the clear filtrate being collected in a 500 c.c. flask, washed with cooled distilled water and made up to mark. At this stage the filtrate (A) is ready for the estimation of glucose in cane leaves.

For the estimation of disaccharides in leaves 100 c.c. of the filtrate (A) is treated with 10 gm. of citric acid and kept for 18 to 24 hours for complete hydrolysis to glucose. The solution is then treated with fairly strong caustic soda until it is slightly alkaline (using litmus paper as an indicator) and then completely neutralised with a drop or two of dilute hydrochloric acid. This solution is then made up to 200 c.c. (referred subsequently as B) and total sugars are estimated as glusose.

In both permanganate and the iodine sulphate methods 50 c.c. of the extracted solution (A or B) are boiled with 50 c.c. of copper sulphate solution spcially made for these reactions and the reduced copper thus formed is dissolved and titrated against N/20 $KMnO_4$ or N/10 $Na_2S_2O_3$, the values for glucose being obtained from appropriate graphs.

In the potassium ferricyanide method the procedure is similar to that described by the authors (*loc. cit.*) earlier and it consists in taking 5 c.c. of 1% potassium ferricyanide solution (previously standardised against extra-pure glucose solution) from burette in a 150 c.c. Erl nmeyer flask and adding to it 2 c.c. of 5% caustic potash and a drop of 1% methylene blue as an internal indicator shortly before the end-point is reached. Into this cold solution is run from the burette containing extracted solution (A or B ready for the glucose estimation) roughly half the total quantity of sugar solution required for complete titration and the flask is heated to boilng on wire-gauze over a flame. After each boiling the flame is lowered to permit of more solution being added from the burette and this process

is repeated till the entire fluid in the flask is decolourised when reading for the quantity of sugar solution used is taken. The glucose percentage can then be directly estimated as 1 c.c. of 1% potassiun ferricyanide solution is equivalent to 1 mgm. of glucose.

3. Results Obtained

In the standard methods glucose is estimated indirectly as pointed out above from the graphs (*loc. cit.*) which were prepared (Fig. 1) from the data

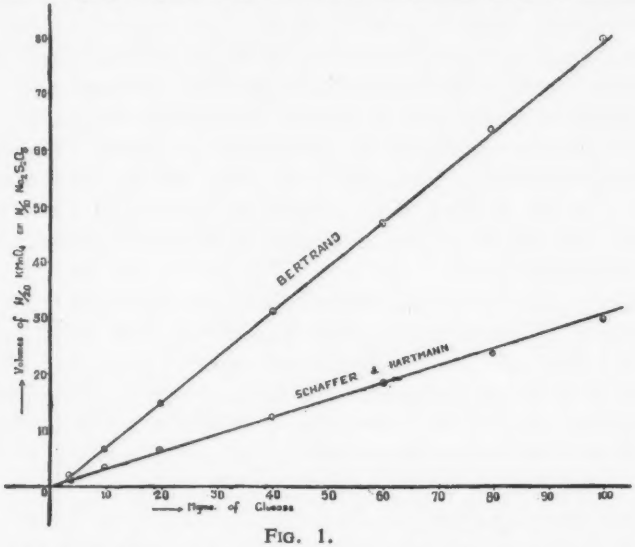

FIG. 1.

(Table I) obtained during these experiments for the estimation of glucose from the titration values.

TABLE I

Quantities of glucose in mgm. taken for the experiment	Volume of N/20 $KMnO_4$ required for neutralisation	Volume of N/10 $Na_2S_2O_3$ required for neutralisation	Remarks
4·0	1·65	1·10	The mean results of 4 readings tabulated
10·0	6·50	3·20	
20·0	14·70	6·30	
40·0	31·00	12·50	
60·0	47·00	18·40	
80·0	63·40	23·40	
100·0	80·20	29·40	

The comparative results of glucose estimation by the three methods are given in Table II. Duplicate estimations were made by each method for each of the twenty-five varieties of leaves under study.

TABLE II

Comparative results of Glucose Estimations by the three methods

Sl. No.	Leaves of the varieties	Age of the plant	Alcoholic soluble matter	Bertrand's				Schaffer and Hartmann				Potassium Ferricyanide			
				Volume of N/20 $KMnO_4$		% Glucose		Volume of N/10 $Na_2S_2O_3$		% Glucose		Volume of 'A' or 'B'		% Glucose	
				I	II	I	II	I	II	I	II	I	II	I	II
						Glucose alone—Solution 'A'									
		days													
1	Co 213	360	9·84	3·5	3·5	0·787	0·787	2·1	2·1	0·738	0·738	36·3	37·5	0·759	0·733
2	,,	,,	9·70	4·5	4·7	0·845	0·886	2·2	2·6	0·833	0·920	29·8	30·0	0·926	0·921
3	,,	120	8·29	6·4	6·6	1·111	1·128	3·2	3·4	1·111	1·193	21·8	21·8	1·261	1·261
4	,,	,,	8·15	7·9	8·2	1·300	1·344	3·9	4·2	1·383	1·468	19·75	19·45	1·395	1·379
5	,,	50	6·65	2·9	3·5	0·616	0·700	1·9	2·1	0·667	0·744	40·0	40·2	0·687	0·686
6	,,	,,	7·27	2·5	3·0	0·561	0·633	1·7	1·9	0·633	0·694	45·0	44·8	0·611	0·614
7	Co 299	120	7·83	10·5	11·0	1·655	1·722	4·5	4·7	1·589	1·667	17·8	17·4	1·545	1·581
8	,,	,,	..	10·8	11·0	1·525	1·550	4·7	5·0	1·500	1·590	17·4	17·8	1·581	1·546
9	Co 313	360	6·37	6·6	6·9	1·122	1·167	3·5	3·8	1·233	1·355	20·3	20·0	1·358	1·375
10	,,	,,	5·78	7·5	7·9	1·244	1·300	4·0	3·8	1·422	1·333	19·6	19·8	1·403	1·390
11	,,	120	6·83	4·8	5·0	0·878	0·905	2·3	2·5	0·817	0·889	30·0	30·4	0·915	0·909
12	,,	,,	..	4·9	5·0	0·805	0·815	2·6	2·7	0·826	0·864	29·0	29·2	0·854	0·848
13	Co 356	,,	6·62	3·4	3·3	0·683	0·672	1·8	2·0	0·639	0·694	40·8	40·9	0·674	0·672
14	,,	,,	..	4·0	3·3	0·690	0·600	2·3	1·9	0·680	0·600	35·1	35·2	0·705	0·703
15	Co 419	,,	..	5·3	5·5	0·852	0·875	2·6	2·4	0·830	0·765	27·0	28·0	0·900	0·884
16	,,	,,	6·65	5·2	4·6	0·933	0·850	2·35	2·6	0·822	0·911	32·2	31·2	0·852	0·863
						After inversion—Solution 'B'									
17	Co 299	120	7·83	7·7	7·4	2·546	2·467	3·6	3·3	2·560	2·330	21·8	21·3	2·524	2·584
18	,,	,,	..	7·8	7·3	2·320	2·191	3·5	3·7	2·230	2·340	21·1	21·5	2·346	2·305
19	Co 313	360	6·37	10·75	10·8	3·626	3·655	4·75	4·90	3·356	3·466	16·0	15·7	3·438	3·514
20	,,	,,	5·78	10·0	10·5	3·178	3·326	4·75	4·75	3·356	3·356	16·0	16·3	3·438	3·377
21	,,	120	6·83	4·4	4·0	1·640	1·533	2·2	2·4	1·560	1·711	32·6	33·0	1·689	1·668
22	,,	,,	..	2·7	3·0	1·0600	1·130	1·8	1·9	1·150	1·200	41·6	42·1	1·190	1·176
23	Co 356	,,	6·62	4·8	5·0	1·755	1·811	2·6	2·5	1·844	1·778	30·3	30·1	1·816	1·827
24	Co 419	,,	6·65	5·6	5·3	1·990	1·890	2·8	2·5	1·990	1·770	28·4	27·7	1·940	1·984
25	,,	,,	..	6·3	6·2	1·950	1·930	3·2	3·1	2·040	1·980	24·6	24·7	2·013	2·004

It has been possible to eliminate the varietal differences as exhibited in their glucose contents. The following Table III gives the variances in each method due to varieties and those within a variety. The latter shows the variances due to laboratory errors.

TABLE III

Sl. No.	Sources of error	D.F.	Permanganate method A	Thiosulphate method B	Ferricyanide method C
1	Mean squares between varieties	24	1·3009	1·2359	1·2789
2	Mean squares within a variety	25	0·00236	0·00510	·00044
3	Observational errors		± ·0486	±0·0714	±0·02095
4	General mean 50 values of glucose %		1·4308	1·4433	1·4723
5	Errors of observation as a percentage of the mean		3·401	4·949	1·423

It is apparent from the above table that the three methods do not differ in the mean values but they differ appreciably in their errors of observation. The potassium ferricyanide method gives the least error, *i.e.*, 1·423% whereas the other methods give 3·401% and 4·949% respectively. Thus as regards precision ferricyanide method is much superior to the other two standard methods.

4. Summary

1. A method for the quick estimation of carbohydrates in cane leaves is described and it consists in the direct use of lead oxlate filtrate for the titration of glucose with 1% alkaline potassium ferricyanide solution.

2. This method is shown to be simpler, quicker and more economical than the standard methods of Bertrand and Schaffer and Hartmann.

3. The three methods are shown to give excellent comparable results for glucose in cane leaves while the new method gives the least observational error thus adding to the precision of results.

5. Acknowledgements

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THE THEORY OF PARTICLES OF SPIN HALF AND THE COMPTON EFFECT: ERRATUM.

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In a recent paper with the above title we pointed out that the energy denominators in the quantum mechanical formulæ for any second order process have exactly opposite signs on the original single electron Dirac theory and the "hole" theory for those transitions to the final state which take place *via* the negative energy states. From this we concluded that the probabilities for second order processes are different on the single electron Dirac theory and the 'hole' theory. Dr. R. C. Majumdar has pointed out to us in a letter, for which we are very grateful to him, that if the calculation be done on the hole theory by the method of the second quantization, then an extra negative sign multiplies the products of the matrix elements for just those transitions which take place *via* the negative energy states, and which just compensates the reversal in sign of the energy denominators of these terms pointed out by us. Since all results which can be derived by the method of the second quantization can also be derived by the configuration space method taking the wave function to be antisymmetrical in the co-ordinates of all the electrons, and the two methods are mathematically equivalent, we have rechecked our calculation which was done by the configuration space method. We find that we overlooked a reversal in sign for just those transitions which take place *via* the negative energy states. The existence of this extra negative sign on the 'hole' theory can be seen quite easily as follows. For those transitions which take place *via* the positive energy states, the electron initially in the positive energy state jumps to the final state of positive energy, the (unobservable) electrons in the negative energy states remaining unaffected. For the transitions *via* the negative energy states, on the other hand, one of the negative energy electrons jumps into the final state of positive energy while the electron initially in the positive energy state jumps into the vacant negative energy state. Thus for those transitions which take place *via* the negative energy states the electron initially in the positive energy state changes places with one of the electrons in negative energy states, and the matrix element suffers a reversal of sign due to the antisymmetry of the wave functions in the co-ordinates of the two particles.

To see this mathematically it is sufficient to consider the transitions *via* the intermediate states I and II′ of (9) of our previous paper. We need then only consider two electrons, namely, one in the positive energy state e (0) and one in the negative energy state [e (k_0)], and ignore all the other electrons in negative energy states. Denoted by $\psi_{p\pm}(x)$ the wave function of an electron of momentum p in a positive or a negative energy state respectively. Then the initial wave function for the two electrons whose co-ordinates are denoted by x_1 and x_2 is

$$\psi_{0+,\,k_0-}(x_1,\,x_2) \equiv \frac{1}{\sqrt{2}}\left\{\psi_{0+}(x_1)\,\psi_{k_0-}(x_2) - \psi_{k_0-}(x_1)\,\psi_{0+}(x_2)\right\}.$$

In the intermediate state I the wave function is correspondingly $\psi_{k_0+,k_0-}(x_1,\,x_2)$, in the state II′ $\psi_{o+,p+}(x_1,\,x_2)$, and in the final state $\psi_{p+,\,k_0-}(x_1,\,x_2)$, where $\mathbf{p} = \mathbf{k_0} - \mathbf{k}$. The interaction $\mathcal{J}$ of the electrons with the radiation field is the usual one, and is such that only one electron jumps at a time. The matrix element for the transition from the initial to the intermediate state I due to the interaction $\mathcal{J}$ with the radiation field is

$$\int \bar{\psi}_{k_0+,k_0-}(x_1,\,x_2)\,\mathcal{J}\,\psi_{o+,k_0-}(x_1,\,x_2)\,d\,x_1\,d\,x_2 = (\bar{U}_{E'}\,\alpha_0\,U_m)$$

in the notation of our previous paper. Similarly the matrix element for the transition from the state I to the final state is

$$\int \bar{\psi}_{p+,k_0-}(x_1,\,x_2)\,\mathcal{J}\,\psi_{k_0+,k_0-}(x_1,\,x_2)\,dx_1\,dx_2 = (\bar{U}_E\,\alpha\,U_{E'}).$$

The matrix element for the transition to the intermediate state II′ is

$$\int \bar{\psi}_{o+,p+}(x_1,\,x_2)\,\mathcal{J}\,\psi_{o+,k_0-}(x_1,\,x_2)\,dx_1\,dx_2 = (\bar{U}_E\,\alpha\,U_{-E'}),$$

and from the state II′ to the final state it is

$$\int \bar{\psi}_{p+,k_0-}(x_1,\,x_2)\,\mathcal{J}\,\psi_{o+,p+}(x_1,\,x_2)\,dx_1\,dx_2$$

$$= -\int \bar{\psi}_{p+,k_0-}(x_1,\,x_2)\,\mathcal{J}\,\psi_{p+,o+}(x_1,\,x_2)\,dx_1\,dx_2 = -(\bar{U}_{-E'}\,\alpha_0\,U_m).$$

It is the above reversal in sign due to the antisymmetry of the wave functions that we unfortunately overlooked in our previous paper. The product

of the two matrix elements for the transition *via* the state II′ is therefore

$$-(\bar{U}_E\, a\, U_{-E'})\,(\bar{U}_{-E'}\, a_0\, U_m),$$

and is exactly -1 times the product that would be obtained on the original Dirac theory. The negative sign in front of the above expression just compensates the fact that the sign of the energy denominator for this term on the hole theory is opposite to that on the original Dirac theory. As a result, in (14) of our previous paper, the positive signs in front of the second and fourth terms are always to be taken, irrespective of whether the calculation is done on the original Dirac theory or on the hole theory. Hence, contrary to our previous statement, the original Dirac theory and the hole theory give exactly the same probabilities for all second order processes, but the reason for this is *not* the one usually given, that the matrix elements for the transitions *via* the negative energy states are the same on the two theories but that the sign of one of the two matrix elements is reversed, this reversal of sign compensating the reversal of sign of the energy denominator.

CALCULATIONS ON THE CASCADE THEORY WITH COLLISION LOSS

By H. J. Bhabha, F.R.S., and S. K. Chakrabarty

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In a recent paper* we gave an exact solution of the equations of the cascade theory assuming the radiation and pair creation processes to be described by the Bethe-Heitler cross-sections for complete screening and taking the collision loss β to be independent of the energy. The solution is in the form of an infinite series, but unlike all the previous solutions, it is *not*, a simple series in powers of the collision loss β, since β enters essentially into the expression for each term. The solution satisfies the physically required boundary conditions at the surface of the layer exactly, whereas the previous treatments of collision loss given by Snyder (1938) and Serber (1938), and following them Corben (1941), are all faulty inasmuch as their solutions do not satisfy the correct boundary conditions at the surface. Moreover the method used by these authors for calculating the total number of particles is mathematically fallacious, so that the numerical results obtained by them must be regarded as uncertain.† Besides this their method is unsuitable for calculating the energy spectrum of particles in a shower near and below the critical energy.

The solution of our previous paper has the advantage that it is particularly suited for obtaining numerical results, since the series is so rapidly convergent that it is sufficient in general to calculate the first term only. Even the second term is small compared with the first both for particles above and below the critical energy, except at thicknesses so large that the cascade has been almost completely absorbed. Thus the first term alone gives to a very good approximation the whole energy spectrum of particles in a cascade from the lowest to the highest energies. In particular it shows that the energy spectrum at small thicknesses, where our method is particularly good, is quite different from what has been generally supposed and differs completely from the spectrum given by Arley (1938) which is based on inadequate physical assumptions.

In this paper we use the solution of the previous paper for calculating the total number of particles of all energies at any depth produced by a primary

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* Communicated to the Royal Society and referred to in this paper as A.

† A detailed discussion of their solution is given in A.

of given energy. Since the publication of the previous paper may be very considerably delayed due to the conditions of war, it is necessary to recapitulate briefly the results obtained there in order to proceed further with the work of this paper.

The Solution of the Equations of the Cascade Theory

We treat the creation of the cascade as a one-dimensioned problem. As usual, we measure all lengths t in a substance in terms of a characteristic unit l defined by

$$l^{-1} = 4\,\frac{Z^2N}{137}\left(\frac{e^2}{mc^2}\right)^2 \log 183\, Z^{-1/3},$$

where Z is the atomic number and N the number of atoms per unit volume. The other symbols have their usual meaning. The collision loss is assumed to be independent of the energy of the electron, and we write

$$-\left(\frac{\partial E}{\partial t}\right)_{coll.} = \beta. \tag{1}$$

The critical energy, introduced in the previous papers, namely the energy of an electron for which its collision and radiation losses are equal, is very nearly equal to β, and for the purposes of this paper will be defined as exactly equal to β. The values of l and β in different substances are given in Table I.

TABLE I

	Air	H_2O	Al	Fe	Pb
l in cm. ..	34200	43·4	9·80	1·84	6·525
Collision loss in M.c.V. ..	103·0	114·6	55·56	25·88	6·927

Define a function

$$R_0(\epsilon) \equiv 1 - a'(\epsilon - \epsilon^2), \tag{2}$$

where $a' = \frac{4}{3} + a$ and $a = 1/9 \log 183\, Z^{-1/3}$. The constant $a = 0{\cdot}06$ in Pb and is less in elements of smaller atomic number. It could be neglected with an error of not more than 6%. According to Bethe and Heitler (1934) the probability that in travelling a distance dt an electron of energy E emits a quantum of energy lying between E′ and E′ + dE' is for complete screening given by

$$R_0\left(\frac{E}{E'}\right)\frac{E'\,dE'\,dt}{E^2}, \tag{3 a}$$

while the probability that a quantum of energy E creates an electron pair of which one particle has an energy between E′ and E′ + dE' is

$$R_0\left(\frac{E'}{E}\right)\frac{dE'\,dt}{E}. \tag{3 b}$$

Let $P(E, t)\,dE$ denote the number of particles (electrons plus positrons) of energies between E and $E + dE$ at a depth t below the surface of the layer due to an electron of energy E_0 incident normally on the surface of the layer, and let $Q(E, t)$ be the corresponding function for the number of quanta. The problem is to calculate the function $P(E, t)$ assuming that at $t = 0$

$$P(E, 0) = \delta(E - E_0), \tag{4}$$
$$Q(E, 0) = 0,$$

corresponding to the incidence of one electron of energy E_0 and no quanta on the surface of the substance. We take the creation and absorption of the cascade to be governed by the three processes described by (1), (3 *a*) and (3 *b*). Our method makes use of the Mellin Transformation first employed in this connection by Landau and Rumer (1938) and in consequence three functions $A(s)$, $B(s)$, $C(s)$ of a variable s, and a constant D are introduced, defined by

$$A_s = \alpha' \left\{\frac{d}{ds} \log \Gamma(s) + \gamma - 1 + \frac{1}{s}\right\} + \frac{1}{2} - \frac{1}{s(s+1)} \tag{5 a}$$

$$B_s = 2\left\{\frac{1}{s} - \alpha' \frac{1}{(s+1)(s+2)}\right\} \tag{5 b}$$

$$C_s = \frac{1}{s+1} + \alpha' \frac{1}{s(s-1)} \tag{5 c}$$

$$D = \frac{7}{9} - \frac{1}{6}\alpha = 1 - \frac{1}{6}\alpha'. \tag{5 d}$$

γ is the Euler-Mascheroni constant. Through the Mellin Transform A_s is connected with the change in the energy spectrum of the particles due to radiation loss, B_s that due to pair creation, while C_s and D are connected with the change in the spectrum of quanta due to radiation loss and pair creation respectively. The functions have no singularities for $R(s) > 1$. Two further functions of s, namely λ_s and μ_s defined by

$$\lambda_s = \tfrac{1}{2}(A_s + D) - \tfrac{1}{2}\sqrt{(A_s - D)^2 + 4\,B_sC_s} \tag{6 a}$$

$$\mu_s = \tfrac{1}{2}(A_s + D) + \tfrac{1}{2}\sqrt{(A_s - D)^2 + 4\,B_sC_s} \tag{6 b}$$

enter directly into the solution. $\mu_s > \lambda_s$ for real $s > 1$. λ_s and μ_s also have no singularities for $R(s) > 1$. Due to the singularities in (5 *c*) and the gamma function in (5 *a*), λ and μ are singular for $= 1, 0$ or a negative integer. The values of λ and μ are given in Table II of A for real s from 1 to 6 at intervals of 0·1.

It was shown in A that an exact solution of the equations of the cascade theory on the assumptions (1) and (3) can be written in the form

$$P(E, t) = P_0(E, t) + P_2(E, t) + P_3(E, t) + \cdots \tag{7}$$

where

$$P_0(E, t) = \frac{1}{2\pi i E_0} \int_{\sigma - i\infty}^{\sigma + i\infty} \left\{ \frac{E_0}{E + \beta g(s, t)} \right\}^s f_0(s, t)\, ds \tag{8}$$

$$P_2(E, t) = \frac{1}{2\pi i E_0} \left(\frac{\beta}{E_0}\right)^2 \int_{\sigma - i\infty}^{\sigma + i\infty} \left\{ \frac{E_0}{E + \beta g(s, t)} \right\}^s f_2(s, t)\, ds \tag{9}$$

etc. σ is a real number greater than 1. The term which would be denoted by $f_1(s, t)$ is exactly zero, and hence $P_1(E, t) = 0$. It is clear that (7) is not a simple series in powers of β since β enters explicitly in the integrand of each term. At $t = 0$ the functions g and f satisfy the boundary conditions

$$\left.\begin{aligned} g(s, 0) &= 0 \\ \left\{\frac{\partial g(s, t)}{\partial t}\right\}_{t=0} &= 1 \end{aligned}\right\} \tag{10 a}$$

$$\left.\begin{aligned} f_0(s, t) &= 1 \\ \left\{\frac{\partial f_0(s, t)}{\partial t}\right\}_{t=0} &= -A_s \end{aligned}\right\} \tag{10 b}$$

$$\left.\begin{aligned} f_n(s, t) &= 0 \\ \left\{\frac{\partial f_n(s, t)}{\partial t}\right\}_{t=0} &= 0 \end{aligned}\right\} \tag{10 c}$$

for $n > 1$, whence it follows that (7) satisfies the boundary condition (4) exactly.

It was shown in A that

$$f_0(s, t) = \frac{D - \lambda_s}{\mu_s - \lambda_s} e^{-\lambda_s t} + \frac{\mu_s - D}{\mu_s - \lambda_s} e^{-\mu_s t} \tag{11}$$

$$g(s, t) = \left[\frac{(D - \lambda_s)^2 e^{-\lambda_s t}}{(\mu_s - \lambda_s)(\lambda_{s+1} - \lambda_s)(\mu_{s+1} - \lambda_s)} + \frac{(D - \lambda_{s+1})^2 e^{-\lambda_{s+1} t}}{(\mu_{s+1} - \lambda_{s+1})(\lambda_s - \lambda_{s+1})(\mu_s - \lambda_{s+1})} \right.$$
$$\left. - \frac{(D - \mu_s)^2 e^{-\mu_s t}}{(\mu_s - \lambda_s)(\lambda_{s+1} - \mu_s)(\mu_{s+1} - \mu_s)} - \frac{(D - \mu_{s+1})^2 e^{-\mu_{s+1} t}}{(\mu_{s+1} - \lambda_{s+1})(\lambda_s - \mu_{s+1})(\mu_s - \mu_{s+1})} \right] \cdot$$
$$\left\{ \frac{D - \lambda_s}{\mu_s - \lambda_s} e^{-\lambda_s t} + \frac{\mu_s - D}{\mu_s - \lambda_s} e^{-\mu_s t} \right\}^{-1}. \tag{12}$$

Since C_s is singular at $s = 1$, while A_s and B_s are not, it follows from (6) that as $s \to 1$ from the right along the real axis

$$\lambda_s \to -\sqrt{2\alpha' D} \cdot (s - 1)^{-\frac{1}{2}}$$

and

$$\mu_s \to \sqrt{2\alpha' D} \cdot (s - 1)^{-\frac{1}{2}}.$$

Hence the first terms in the numerator and denominator of (12) dominate and

$$g(s, t) \to (2\alpha' D)^{-\frac{1}{2}} (s-1)^{\frac{1}{2}} \tag{13}$$

as $s \to 1$ from the right along the real axis. It was shown in A that as $s \to \infty$

$$g(s, t) \to \begin{cases} \dfrac{2}{\alpha' \log s} & \text{for } \alpha' t > 2 \\ t & \text{for } \alpha' t < 2. \end{cases} \tag{14}$$

Thus for $t > 2/\alpha'$, as s increases along the real axis from 1, $g(s, t)$ increases from zero, reaches a maximum value of the order 1 for $s \sim 3{\cdot}3$ and then tends to zero as $s \to \infty$. For $t < 2/\alpha'$ it increases from zero and tends to t as $s \to \infty$. Table II displays this behaviour of $g(s, t)$. The

TABLE II

Values of g (s, t) *for different values of* s *and* t

s \ t	1·0	1·3	1·5	2·0	4·0	10·0	∞
1·5	·4892	·5113	·5174	·5269	·5353	·5364	·5364
2·0	·6309	·7071	·7155	·7705	·8009	·8186	·8186
2·5	·7264	·8298	·8759	·9339	·9564	·9993	1·013
3·0	·7738	·9035	·9659	1·048	1·037	1·083	1·141
3·5	·8054	·9545	1·029	1·129	1·066	1·094	1·226
4·0	·8317	·9949	1·079	1·189	1·064	1·067	1·292
4·5	·8475	1·023	1·116	1·239	1·047	1·027	1·350
5·0	·8630	1·050	1·149	1·287	1·027	·9876	1·386

general dependence of $g(s, t)$ on t for fixed s is equally simple. From (10 *a*) it follows that for small t

$$g(s, t) \sim t, \tag{15}$$

and it rapidly tends to some constant limiting value as $t \to \infty$. This limiting value is about 0·5 for $s = 1{\cdot}5$, 0·8 for $s = 2$ and about 1 for s between 2·5 and 3·0. (14) shows that for large s there is a dip in $g(s, t)$ for $t \sim 2/\alpha'$, but the values of s for which this dip is pronounced are large and not of physical importance.

Since $\mu_s > \lambda_s$ for real $s > 1$ it follows that for all except very small t the second term in (11) makes a contribution to (8) which is negligible compared with the first. As shown in A, the contribution of the first term in (11) to the integral (8) can be evaluated by the saddle point method with an error less

than five per cent. The method is similar to that used below for calculating the total number of particles. The saddle point s_0 depends on E and t. By differentiating (8) with respect to t it appears that the maximum of (8) for a given E occurs when t is such that at the saddle point $\lambda_s \simeq 0$. From (5) and (6) it can be shown that $\lambda_s = 0$ when $s = 2$. Hence at the maximum the saddle point lies at $s_0 = 2$. As shown in A, $s_0 < 2$ for smaller thicknesses before $P(E, t)$ has reached its maximum, and $s_0 > 2$ after the maximum. For every small t the contribution of the second term in (11) to (8) is as important as the first and then the saddle point method cannot be employed. Another method of calculating (7) in this case was given in A.

The properties of the function $g(s, t)$ are of direct physical importance in determining the spectrum and the total number of particles. For small t, remembering (15), we see that E only appears in (7) in the combination $E + \beta t$, showing that the whole spectrum is shifted down by an amount βt, corresponding to the energy lost by each particle by collision in the thickness t. For thicknesses which are not very small, Table II shows that $g(s, t)$ is about 0·5 for $s = 1{\cdot}5$, 0·8 for $s = 2{\cdot}0$, and 1 for s between 2·5 and 4·0. Thus for not too small t, the spectrum starts getting flat for $E \lesssim 0{\cdot}5\,\beta$ at thicknesses before the shower has reached its maximum, for $E \lesssim 0{\cdot}8\,\beta$ at the maximum, and for $E \lesssim \beta$ after the maximum.

Now consider $P_2(E, t)$ given by (9). As shown in A,

$$f_2(s, t) = m_s\, e^{-\lambda_{s-2} t} + f_2'(s, t) \tag{16}$$

where $f_2'(s, t)$ is a sum of terms containing exp. $(-\lambda_{s-1} t)$, exp. $(-\lambda_s t)$, exp. $(-\mu_{s-2} t)$, exp. $(-\mu_{s-1} t)$ and exp. $(-\mu_s t)$ as factors.

$$m_s = (s-1)(s-2)\frac{(D-\lambda_{s-2})^3}{(\mu_{s-2}-\lambda_{s-2})(\lambda_{s-1}-\lambda_{s-2})^2(\mu_{s-1}-\lambda_{s-2})^2}\left\{\frac{(\lambda_{s-1}-\lambda_{s-2})(\mu_{s-1}-\lambda_{s-2})}{(\lambda_s-\lambda_{s-2})(\mu_s-\lambda_{s-2})} - \frac{1}{2}\right\} \tag{17}$$

Similarly $f_n(s, t)$ of the nth term contains exp. $(-\lambda_{s-n} t)$, exp. $(-\lambda_{s-n+1} t)$, etc.

Writing s for $s-2$ in (9) and shifting the path of integration to the right so that σ again has its original value, we get

$$P_2(E, t) = \frac{1}{2\pi i\, E_0}\int_{\sigma-i\infty}^{\sigma+i\infty}\left\{\frac{E_0}{E+\beta g(s+2, t)}\right\}^s\left\{\frac{\beta}{E+\beta g(s+2, t)}\right\}^2 f_2(s+2, t)\, ds \tag{18}$$

$P_n(E, t)$ may be transformed correspondingly by writing s for $s-n$ and shifting the contour to the right so that σ has again its original value. When written in this form, only λ_{s+r} and μ_{s+r}, where r is zero or a positive integer, appear in the integrand of each term and λ_{s-1}, λ_{s-2}, etc., are entirely avoided. Since λ_s and μ_s have singularities for $s = 1$, 0 or a negative integer, this is a better

way of writing the solution.* Since by (5) and (6 a), $\lambda_s < \lambda_{s+1} < \lambda_{s+2}$ for real $s > 1$, it follows that except for small t the contribution to P_2 due to the first term on the right-hand side of (16) is much greater than that of the second. Thus, for all except small t,

$$P_2(E, t) = \frac{1}{2\pi i\, E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left\{\frac{E_0}{E+\beta g(s+2, t)}\right\}^s \left\{\frac{\beta}{E+\beta g(s+2, t)}\right\}^2 m_{s+2}\, e^{-\lambda_s t}\, ds \quad (19)$$

The integral (19) can be calculated to the same degree of accuracy as (8) by the saddle point method. It was shown in A that it is usually small compared with (8) even for values of E less than β. The first term (8) of the series (7) therefore gives the whole energy spectrum above and below the critical energy with considerable accuracy. The contribution to $P_2(E, t)$ due to the term containing exp. $(-\lambda_{s+1} t)$ as a factor in $f_2'(s+2, t)$ is smaller than (19) by a factor β/E_0 and is hence negligible for $E_0 \gg \beta$. The other terms in $f_2'(s, t)$ make an even smaller contribution. When $E_0 < \beta$, it can be shown that the effect of $f_2'(s, t)$ is to largely cancel the contribution of the first term in (16) to $P_2(E, t)$, thus making the total magnitude of $P_2(E, t)$ still smaller in relation to $P_0(E, t)$. Indeed for $E_0 \ll \beta$, the cascade must be completely stopped in a distance $t \ll 1$ due to collision loss alone. It can then be shown that the contributions of all the terms in (7) are quite negligible compared with the first, which can now be worked out accurately as has been done in A without using the saddle point method.

To get the number $N(E, t)$ of particles of energy greater than E we must integrate (7) over all energies from E to infinity. Thus

$$N(E, t) = N_0(E, t) + N_2(E, t) + N_3(E, t) + \cdots \quad (20)$$

where

$$N_0(E, t) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \left\{\frac{E_0}{E+\beta g(s, t)}\right\}^{s-1} \frac{1}{s-1} f_0(s, t)\, ds, \quad (21)$$

etc. The resulting integrals can also be evaluated by the saddle point method. To get the total number of particles at a given depth t we must put $E = 2mc^2$, the lowest energy for which the pair creation process can still take place. As mentioned earlier, $g(s, t)$ is of the order unity for all except small t. Now Table I shows that even in lead $\beta \gg 2mc^2$, and for light elements like air β is still greater. To obtain the total number $N(t)$ of particles in a shower

* K. S. K. Iyengar has given another equivalent form of writing our solution namely,

$$P_n(E, t) = \frac{1}{2\pi i\, E_0} \int_{\sigma-i\infty}^{\sigma+i\infty} \left\{\frac{E_0}{E+\beta g(s, t)}\right\}^s \left\{\frac{\beta}{E+\beta g(s, t)}\right\}^n \phi_n(s, t)\, ds$$

Here $\phi_0(s, t) = f_0(s, t)$ and $\phi_2(s, t) = f_2(s+2, t)$, while $\phi_n(s, t)$ for $n > 2$ are linear combinations of the $f_n(s+n, t)$ multiplied by functions of $g(s, t)$.

we may therefore put $E = 0$, and get

$$N(t) = N_0(t) + N_2(t) + N_3(t) + \qquad (22)$$

where $N_0(t)$ is got by putting $E = 0$ in (21), and

$$N_2(t) = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\left\{\frac{E_0}{\beta g(s+2,t)}\right\}^{s-1}\frac{1}{\{g(s+2,t)\}^2}\frac{1}{s+1}f_2(s+2,t)\,ds \qquad (23)$$

and so on.

First consider (21). For all but small t the main contribution comes as before from the first term of f_0 given by (11). Introduce a variable y_0 defined by

$$y_0 = \log\frac{E_0}{\beta} \qquad (24)$$

and write the integrand of (21) as exp. $\psi(E, s)$ where

$$\psi(E,s) \equiv (s-1)\,y_0 - \lambda_s\,t + \log\frac{D-\lambda_s}{\mu_s-\lambda_s} - \log(s-1) - (s-1)\,G \qquad (25)$$

and $$G \equiv \log\left\{\frac{E}{\beta} + g(s,t)\right\}.$$

The saddle point s_0 is determined by

$$\psi'(E,s) \equiv y_0 - \lambda'_{s_0}\,t + \left\{\frac{d}{ds}\log\frac{D-\lambda_s}{\mu_s-\lambda_s} - \frac{1}{s-1} - G - (s-1)\,G'\right\}_{s=s_0} = 0, \qquad (26)$$

where a dash denotes differentiation with respect to s. Hence, by the saddle point method,

$$N_0(E,t) = \left\{\frac{E_0}{E+\beta g(s_0,t)}\right\}^{s_0-1}\frac{1}{s_0-1}\frac{D-\lambda_{s_0}}{\mu_{s_0}-\lambda_{s_0}}\frac{e^{-\lambda_{s_0}t}}{\sqrt{2\pi\,\psi''(E,s_0)}} \qquad (27)$$

$\psi''(E, s_0)$ is a function of s_0 and t but not of y_0. Since $g(s, t)$ is of the order unity, (25) to (27) show that when $E \gg \beta$ the effect of g on the number of particles of energy greater than E becomes negligible. This is what we should expect. It is more important to notice by putting $E = \beta$, that the effect of g is to almost halve the number of particles of energy greater than the critical energy.

To obtain $N_0(t)$ we have only to put $E = 0$ in the formulæ (25) to (27). The numerical values thus obtained for different values of y_0 and t are given in Table III.

The second term (22) can be calculated similarly. We have in fact, from (16)

$$N_2(E,t) = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\left\{\frac{E_0}{\beta g(s+2,t)}\right\}^{s-1}\frac{1}{\{g(s+2,t)\}^2}\frac{1}{s+1}\,m_{s+2}\,e^{-\lambda_s t}\,ds \qquad (28)$$

with m_s given by (17). This can also be calculated by the saddle point method. For comparison we have calculated N_2 for $t = 2$, 4 and 10, and all y_0 from

TABLE III

Values of N_0 (t) *for different values of* y_0 *and* t. *The lower rows for* t = 2, 4 *and* 10 *give the values of* N_2 (t). *These provide an estimate of the error made in taking* N_0 (t) *to give the total number of particles* N (t).

t \ y_0		3	4	5	6	7	8	9	10	12	14	16
2	N_0	3·050	6·214	10·58	17·05	25·64	36·09	49·94	67·13	120·4	283·6	
	N_2	·1414	·1746	·2086	·2662	·3352	·3910	·4481	·5655	·5958		
4	N_0	1·181	4·771	13·78	33·22	69·91	136·5	241·2	422·5	1117	2578	5439
	N_2	·3731	·7146	1·349	2·199	3·510	5·651	8·333	12·26	20·37	42·77	
6	N_0	·3811	2·143	8·633	28·69	80·56	198·4	460·2	969·8	3735	12240	35280
8	N_0	·1180	·8057	4· 035	16·73	58·83	181·3	499·3	1284	6898	29970	107000
10	N_0	·0366	·2800	1·613	7·916	33·26	120·8	392·2	1176	8073	47320	229500
	N_2	·0513	·2340	·8971	3·394	10·49	31·21	80·92	194·7	987·1	4234	15130
12	N_0		·0947	·6029	3·333	16·06	68·19	251·6	859·2	8018	57820	340200
15	N_0		·0165	·1212	·7668	4·453	22·26	98·19	396·3	5080	50300	390800
20	N_0			·0073	·0557	·3830	2·329	12·79	63·35	1268	19040	222400
25	N_0				·0033	·0258	·1843	1·214	7·292	197·8	4171	68340
30	N_0				·0002	·0016	·0125	·0927	·6110	22·37	605·5	13210

3 to 10 at intervals of 1, and also for $y_0 = 12$, 14 and 16. The resulting figures are also given in Table III. They show that N_2 is less than thirty per cent. of N_0 except for $t = 10$ and y_0 less than 7. This is as we should expect, since for y_0 less than 7, $t = 10$ corresponds to a thickness well after the maximum when the cascade is in fact getting absorbed by collision loss. For example, for $y_0 = 3$ and $t = 10$, N_2 is actually somewhat greater than N_0. For this value of y_0 the maximum number of particles occurs at $t \sim 2$, where the number is approximately 3, while at $t = 10$ it has already fallen to 0·03, and is negligible compared with the number at the maximum. Our calculations show, therefore, that for all except the very end of a cascade, the first term $N_0(t)$ alone of the series (22) gives the total number of particles with considerable accuracy. The figures for $N_0(t)$ may therefore be taken to give the total number of particles $N(t)$ with an error which is indicated by $N_2(t)$.

The maximum of $N_0(t)$ occurs as usual* when $\lambda_{s_0} = 0$, that is when $s_0 = 2$. Since at the maximum, $N_2(t)$ is less than 10% of $N_0(t)$, this also gives the maximum of $N(t)$ with considerable accuracy. Putting $E = 0$ and $s_0 = 2$ in (26) we get

$$t_m = 1{\cdot}01\ y_0 - 1{\cdot}57 - 1{\cdot}01 \left\{ \log g(2, t_m) + \frac{d}{ds} \log g(2, t_m) \right\}. \tag{29}$$

As t increases from 2 to ∞, the last term varies from $-{\cdot}32$ to $-{\cdot}38$. Now the saddle point method is only a good approximation if y_0 is not too small. We have only used it for $y_0 \geqslant 3$. Hence with an error less than 5% we could replace the last term by the average of the above two values and write

$$t_m = 1{\cdot}01\ y_0 - 1{\cdot}92. \tag{30}$$

Putting $s_0 = 2$ and $E = 0$ in (27) we get

$$N_{max.} = \frac{e^{y_0 - {\cdot}8365 - \log g(2, t_m)}}{\sqrt{2\pi\, \psi''(0, 2)}}$$

where

$$\psi''(0, 2) = \left\{ -\lambda_s''\, t_m + \frac{d^2}{ds^2} \log \frac{D - \lambda_s}{\mu_s - \lambda_s} + \frac{1}{(s-1)^2} - 2\frac{d}{ds} \log g(s, t_m) - (s-1)\frac{d^2}{ds^2} \log g(s, t_m) \right\}_{s=2}$$

$$= \left\{ 1{\cdot}561\ t_m + 0{\cdot}379 - 2\frac{d}{ds} \log g(s, t_m) - \frac{d^2}{ds^2} \log g(s, t_m) \right\}_{s=2}$$

* The maximum occurs when the derivative of (21) with respect to t vanishes. Since $g(s, t)$ also depends on t, the maximum does not occur exactly when $s_0 = 2$. However, as Table II shows, for $s_0 \sim 2$ and $t > 2$, $g'(s, t) \ll g(s, t)$, and to a high degree of accuracy the saddle point falls at $s_0 = 2$.

Using (29) we get finally

$$\psi''(0, 2) = 1{\cdot}58\left[\log\frac{E_0}{\beta} - 1{\cdot}31 - \log g\,(2, t_m) - 2{\cdot}26\,\frac{d}{ds}\log g\,(2, t_m) - 0{\cdot}633\,\frac{d^2}{ds^2}\log g\,(2, t_m)\right]$$

Hence

$$N_{max.} = 0{\cdot}137\frac{E_0}{\beta g\,(2, t_m)}\left[\log\frac{E_0}{\beta} - 1{\cdot}31 - \log g\,(2, t_m) - 2{\cdot}26\,\frac{d}{ds}\log g\,(2, t_m) - 0{\cdot}633\,\frac{d^2}{ds^2}\log g\,(2, t_m)\right]^{-\frac{1}{2}} \quad (31)$$

As t increases from 2 to ∞ the sum of all the terms except the first in the square brackets of (31) decreases from $-1{\cdot}87$ to $-1{\cdot}93$. Hence with an error less than 3% we may replace (31) by

$$N_{max.} = 0{\cdot}137\frac{E_0}{\beta g(2, t_m)}\left[\log\frac{E_0}{\beta} - 1{\cdot}90\right]^{-\frac{1}{2}}. \quad (32)$$

Table II shows that for $t_m \geqslant 2$, that is, by (30), for $y_0 \geqslant 4$, $g\,(2, t_m) = 0{\cdot}80 \pm 0{\cdot}03$. Hence, for $y_0 \geqslant 4$ we may take $g\,(2, t_m) = 0{\cdot}8$ with an error of less than 4%.

The expression for the total number N (β, t) of particles above the critical energy is got to the same approximation by putting $E = \beta$ in (21). Its maximum is got by putting $E = \beta$ and $s_0 = 2$ in (27). This is equivalent to replacing $g\,(2, t_m)$ in (31) by $1 + g\,(2, t)$, where t is only slightly different from t_m, and is got by replacing $g\,(2, t_m)$ by $1 + g\,(2, t)$ in (29). To the same degree of approximation as (31) we get

$$N_{max.}\,(\beta) = 0{\cdot}137\frac{E_0}{\beta\,\{1 + g\,(2, t)\}}\left[\log\frac{E_0}{\beta} - 0{\cdot}80)\right]^{-\frac{1}{2}} \quad (33)$$

The alteration of the last term in square brackets makes little difference between (32) and (33) since it appears under a square root. Dividing (33) by (32) we see that the number of particles above the critical energy to the total number is in the ratio $g\,(2, t_m)/\{1 + g\,(2, t)\} \simeq 0{\cdot}8\,/1{\cdot}8$. Hence, at the maximum of a cascade, the number of particles above the critical energy is 0·8 times the number below the critical energy. Our considerations therefore justify the very crude assumption originally made by Bhabha and Heitler (1937) that the number of particles below the critical energy is roughly equal to the number above the critical energy. This holds at the maximum of the cascade. Before the maximum the number above the critical energy is relatively somewhat more, and after the maximum somewhat less. The above considerations are not even approximately true for very small, t, for as shown in A, the shape of the spectrum is then quite different. (33) also shows that the number of particles above the critical energy can by no

means be calculated by neglecting collision loss, for this is equivalent to dropping $g(2, t)$ in (33) and leads to a number of particles nearly twice the correct number.

(32) gives the maximum total number of particles produced by a primary of given energy with an accuracy of about 10%. The figures given in Table III for the number of particles before the maximum is reached are more accurate, whereas those after the maximum are less accurate. In general the error of the figures of Table III is certainly less than 30% except for thicknesses so great that the shower has been almost completely absorbed. Especially for small y_0, the error introduced by giving the radiation and pair creation cross-sections their values for complete screening is also of this order. The accuracy of the mathematics is therefore greater than the accuracy of the physical assumptions. The same physical approximations or even cruder ones also underlie the work of all the other authors, except Corben, who has approximately allowed for incompleteness of screening by an empirical method. His treatment of collision loss, however, follows that of Snyder and Serber and is defective. We therefore believe that the figures of Table III are the most accurate that have been given so far.

Summary

A rigorous solution of the equations of the cascade theory taking the radiation and pair creation cross-sections to be those for complete screening and the collision loss to be a constant is given which exactly satisfies the given boundary conditions at the surface of the layer. The solution is in the form of an infinite series but it is not a series in powers of the collision loss β since this enters essentially into the expression for each term. The first term of the series alone gives the whole energy spectrum of cascade electrons both above and below the critical energy with very considerable accuracy. The total number of particles produced at a depth t by an electron of initial energy $E_0 = \beta$ exp. y_0 is given in Table III for t varying from 2 to 30 and y_0 from 3 to 16. It is shown that at the maximum of the cascade the total number of particles above the critical energy is 0·8 times the number below the critical energy.

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7. Snyder .. *Ibid.*, 1938, **53**, 960–65.

Note added in proof:—

As has been mentioned in the text, the solution of the cascade problem given by Serber is mathematically defective. The numerical results derived from his formulæ therefore differ considerably from those of this paper. For example, the total numbers of particles in a cascade at thicknesses t equal to 4 and 6 and three values of y_0 calculated by his method are given in the following table.

Values of N (t) calculated by Serber's method

t \ y_0	3	5	10
4	2·82	21·8	576
6	1·11	16·5	1635

These figures are larger than those given in Table III of this paper by fifty to a hundred per cent. In the next table are given the values of t_m and N_m for different y_0 as calculated respectively from formulæ (30) and (32) of this paper, and formulæ (8) and (9) of Serber's paper. The values of t_m taken from the figures of Carlson and Oppenheimer (C. & O.) are also given for comparison.

Values of t_m *and* N_m

y_0		3	4	5	6	7	8	9	10	12
t_m	Present Paper	1·11	2·12	3·13	4·14	5·15	6·16	7·17	8·18	10·20
	Serber ..	1·55	2·77	3·88	4·94	5·98	7·02	8·04	9·06	11·08
	C. & O. ..	1·83	3·08	4·33	5·58	6·83	8·08	9·33	10·58	13·08
N_m	Present Paper	3·27	6·44	14·4	34·1	83·0	207	520	1323	8754
	Serber	3·92	9·07	21·8	53·8	135	341	873	2246	15090

The table shows that while Serber's formulæ make the maximum of the cascade for a given y_0 occur at a smaller thickness than Carlson and Oppenheimer's, nevertheless the maxima occur at larger thicknesses than those given by the formulæ of this paper, the discrepancy being very considerable for small y_0. Similarly, his formulæ give a value of N_m which is some fifty per cent larger than ours. Our figures would therefore lead to a considerable revision of the estimates of the relative magnitude of the hard component at great heights in the atmosphere, which are based on the differences between the theoretical curves of the cascade theory and the observed atmospheric absorption curves.

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ERRATUM

Vol. XV, No. 3, page 141, in the third of the equations in (15) *omit* the " $=0$ " at the end of the equation.

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